PB80-205255

Comparison of Four Leachate-Generation Procedures for Solid Waste Characterization in Environmental Assessment Programs

GCA Corp.
Bedford, MA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

May 80

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-80-118	2.
3. RECIPIENT'S ACCESSION NO. PB 80 205255	
4. TITLE AND SUBTITLE Comparison of Four Leachate-generation Procedures for Solid Waste Characterization in Environmental Assessment Programs	5. REPORT DATE May 1980
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Daniel E. Bause and Kenneth T. McGregor	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS GCA/Technology Division, 213 Burlington Road, Bedford, Massachusetts 01730	10. PROGRAM ELEMENT NO. 1AB604
	11. CONTRACT/GRANT NO. 68-02-3129, Task 103
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development, Industrial Environmental Research Laboratory, Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final; 5/79-1/80
	14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Frank E. Briden, Mail Drop 62, 919/541-2557.

16. ABSTRACT The report gives results of an evaluation of four leachate-generating procedures in terms of their general applicability, reproducibility, compatibility with environmental assessment methods, and leaching characteristics. The generated leachates were analyzed for nine metals by atomic absorption, and for F(-), Cl(-), and SO4(--) by ion chromatography. Seven energy process wastes (oil shale, FBC waste, two flyashes, boiler slag, scrubber sludge, and hopper ash) were extracted to evaluate the general applicability of the leachate tests. The ASTM methods had the best reproducibility, and the EP method, the poorest. The EP and CAE procedures leached the largest quantities of trace metals from the wastes. However, based on the total metal concentration in the sample, the leachate methods generally extracted < 1%. The EP and ASTM-B methods caused some problems with flameless AA analyses. Based on the RCRA criteria, five of the energy wastes would be classified as hazardous by at least one leachate procedure. Se usually exceeded the threshold value for the leachate. Based on this study, the ASTM-A and CAE procedures are preferred for leachate generation. Regardless of the leachate-generating method selected for waste characterization, the experimental procedure must be defined more precisely with respect to preparation, preservation, and other aspects.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Leaching Wastes Analyzing Properties Assessments Oil Shale Fluidized Bed Processing Combustion Fly Ash Slags Sludge Ashes	Pollution Control Stationary Sources Leachates Solid Waste Characterization Environmental Assessment	13B 07D, 07A 13H 14G 21B 14B 11F, 11B 08G

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

PB80-205255

United States
Environmental Protection
Agency

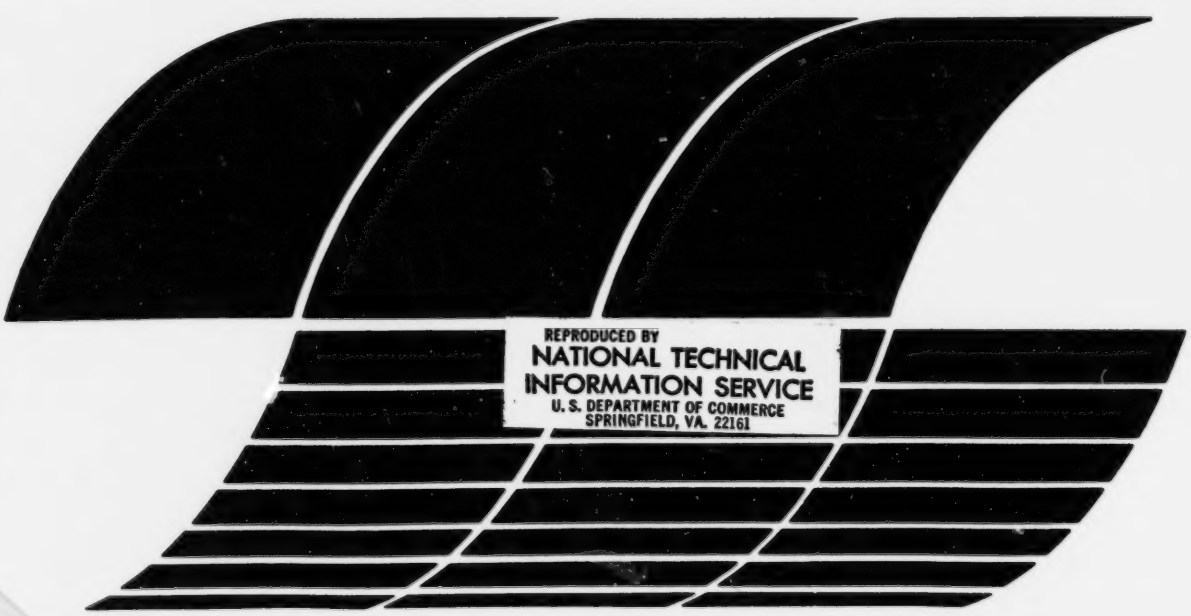
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-80-118
May 1980

EPA

Comparison of Four Leachate-generation Procedures for Solid Waste Characterization in Environmental Assessment Programs

Interagency Energy/Environment R&D Program Report



RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/7-80-118

May 1980

Comparison of Four Leachate-generation Procedures for Solid Waste Characterization in Environmental Assessment Programs

by

Daniel E. Bause and Kenneth T. McGregor

GCA/Technology Division
213 Burlington Road
Bedford, Massachusetts 01730

Contract No. 68-02-3129
Task No. 103
Program Element No. 1AB604

EPA Project Officer: Frank E. Briden

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

DISCLAIMER

This Final Report was furnished to the Environmental Protection Agency by GCA Corporation, GCA/Technology Division, Burlington Road, Bedford, Massachusetts 01730, in fulfillment of Contract No. 68-02-3129, Technical Directive 103. The opinions, findings, and conclusions expressed are those of the authors and not necessarily those of the Environmental Protection Agency. Mention of company or product name is not to be considered as an endorsement by the Environmental Protection Agency.

ABSTRACT

Four leachate procedures were evaluated in terms of their general applicability, reproducibility, Environmental Assessment methods compatibility, and leaching characteristics. The leachates generated by these methods were analyzed for nine metals by atomic absorption methods and by ion chromatography for F^-, Cl^-, and SO_4^{2-}. Seven energy process wastes including oil shale, FBC waste, fly ash, boiler slag, scrubber sludge, and hopper ash were extracted to evaluate the general applicability of the leachate tests. The ASTM methods had the best reproducibility and the EP method had the poorest. The EP and CAE procedures leached the largest quantities of trace metals from the wastes. However, based on the total metal concentration in the sample, the leachate methods generally extracted < 1 percent. The EP and ASTM-B methods caused some problems with flameless AA analyses. Based on the RCRA criteria, five of the energy wastes would be classified as hazardous by at least one of the leachate procedures. Selenium usually exceeded the threshold value for the leachate.

In view of the results obtained in this study, the ASTM-A and CAE are the preferred leachate generation procedures. Regardless of the leachate method selected for waste characterization, the experimental procedure must be defined more precisely with respect to the separation of phases in complex industrial wastes, the preparation of the sample for leaching, the agitation apparatus and rate, and the preservation of the leachate for the subsequent analyses.

CONTENTS

Abstract iii
Figures vi
Tables vi
Acknowledgment xi

1. Introduction 1
2. Summary and Conclusions 3
3. Recommendations 6
4. Overview of Leachate Problem 8
   - Background 8
   - Objectives 9
   - General Considerations for Leachate Generation 13
   - Factors Affecting Concentration in Leachates 14
5. Literature Review 18
   - Previous Reports 18
6. Experimental 38
   - EPA-OSW Extraction Procedure 38
   - ASTM-A Method (Water Extraction) 40
   - ASTM-B Method (Acetate Buffer Extraction) 41
   - Carbonic Acid Extraction 42
   - Atomic Absorption 42
   - Ion Chromatography 43
   - Spark Source Mass Spectrography 43
7. Results and Discussion 45
   - General Applicability of the Leachate Methods 45
   - Leaching Characteristics 50
   - Precision of Leachate Methods 62
   - Variations in Leachate Procedures 72
   - Compatibility with Environmental Assessment Procedures. . 73

References 76
Appendices

A. Tables of Leachate Concentrations of Inorganic Contaminants 78
B. Spark Source Mass Spectrography Data for the EP Leachate of Bituminous Coal Fly Ash No. 1 and the EP Leachate Blank . . 91

Preceding page blank

FIGURES

Number		Page
1	EP extractor	39

TABLES

Number		Page
1	List of Toxic Substances	9
2	Comparison of Experimental Parameters for the ASTM-A, ASTM-B, EP, and CAE Leachate Methods	11
3	Chemical Composition of University of Wisconsin's Synthetic Municipal Landfill Leachate	20
4	Comparison of Three Leaching Tests	20
5	The Number of Times Acid or H_2O Leaching Solutions Gave Highest Concentrations or Release of an Inorganic Parameter From a Waste	22
6	Standard Deviation Calculations for Multiple Replicates of Paint Waste Leached With Synthetic Leachate Using SLT Procedures	23
7	Comparison of Metals Analyses for Sewage Sludge EP Extract	27
8	Trace Elemental Analyses of As-Contaminated Groundwater Sample, EP Extracts, and Blank	28
9	Hazardous Potential Summary	30
10	ICAPS Screening Analysis of EP Extracts: Approximate Elemental Composition of Extracts From Selected Waste Samples	32
11	Average Relative Standard Deviation for AAS Analyses of EP Extracts	33

TABLES (continued)

Number		Page
12	Evaluation of Extraction Procedure (EP): Average Means and Standard Deviations for AAS Analyses of EP Extracts of Wastes From Ponds O and P, Site A	33
13	Quality Control Data: Comparison of Barium Spike Recovery From Selected Samples (Matrices)	34
14	EP Reproducibility	36
15	Description and Analysis of Waste Samples	46
16	Summary of Final pH for Wastes Tested	50
17	Detection Limits for Atomic Absorption and Ion Chromatographic Analyses	52
18	Wastes Classified as Toxic by RCRA Criteria	53
19	Comparison of Leachate Data (In µg/g) for Oil Shale	54
20	Comparison of Leachate Data (In µg/g) for FBC Waste	55
21	Comparison of Leachate Data (In µg/g) for Bituminous Coal Fly Ash No. 1	55
22	Comparison of Leachate Data (In µg/g) for Bituminous Coal Boiler Slag	56
23	Comparison of Leachate Data (In µg/g) for Lignitic Coal Scrubber Sludge	56
24	Comparison of Leachate Data (In µg/g) Generated by the ASTM-A Procedure for Hopper Ash	57
25	Comparison of Leachate Data (In µg/g) Generated by the ASTM-B Procedure for Hopper Ash	57
26	Comparison of Leachate Data (In µg/g) Generated by the Extraction Procedure for Hopper Ash	58
27	Comparison of Leachate Data (In µg/g) Generated by the Carbonic Acid Extraction for Hopper Ash	58
28	Number of Times Each Leachate Test Gave the Highest Concentrations of an Inorganic Contaminant	60

TABLES (continued)

Number		Page
29	Number of Times Each Leachate Test Gave the Largest Quantity (Mass/g of Sample) of an Inorganic Contaminant	60
30	Percentage Leached From the FBC Waste	63
31	Percentage Leached From the Bituminous Coal Fly Ash No. 1	63
32	Percentage Leached From the Bituminous Coal Fly Ash No. 2	64
33	Percentage Leached From the Bituminous Coal Boiler Slag	64
34	Percentage Leached From the Lignite Scrubber Sludge	65
35	Percentage Leached From the Hopper Ash	65
36	Calculation of Relative Standard Error From Results of Hopper Ash Extractions	67
37	Calculation of Relative Standard Error (RSE) for Each Leachate Generated by the ASTM-A Method	68
38	Calculation of Relative Standard Error (RSE) for Each Leachate Generated by the ASTM-B Method	69
39	Calculation of Relative Standard Error (RSE) for Each Leachate Generated by the EP	70
40	Calculation of Relative Standard Error (RSE) for Each Leachate Generated by the CAE Method	71
41	Comparison of Analytical Data (In µg/g) Generated by Variations of ASTM-A Procedure For Oil Shale	73
42	Comparison of Leachate Data (In µg/g) for Bituminous Coal Fly Ash No. 2	74
A-1	Concentrations of Inorganic Species in Oil Shale Leachate Generated by the ASTM-A Method	78
A-2	Concentrations of Inorganic Species in Oil Shale Leachate Generated by Variations of the ASTM-A Method	79
A-3	Concentrations of Inorganic Species in Oil Shale Leachate Generated by the ASTM-B Method	79

TABLES (continued)

Number		Page
A-4	Concentrations of Inorganic Species in Oil Shale Leachate Generated by the EP	80
A-5	Concentrations of Inorganic Species in Oil Shale Leachate Generated by the CAE	80
A-6	Concentrations of Inorganic Species in FBC Waste Leachate Generated by the ASTM-A Method	81
A-7	Concentrations of Inorganic Species in FBC Waste Leachate Generated by the ASTM-B Method	81
A-8	Concentrations of Inorganic Species in FBC Waste Leachate Generated by the EP	82
A-9	Concentrations of Inorganic Species in FBC Waste Leachate Generated by the CAE	82
A-10	Concentrations of Inorganic Species in Bituminous Coal Fly Ash No. 1 Leachate Generated by the ASTM-A Method	83
A-11	Concentrations of Inorganic Species in Bituminous Coal Fly Ash No. 1 Leachate Generated by the ASTM-B Method	83
A-12	Concentrations of Inorganic Species in Bituminous Coal Fly Ash No. 1 Leachate Generated by the EP	84
A-13	Concentrations of Inorganic Species in Bituminous Coal Fly Ash No. 2 Leachate Generated by the ASTM-B Method	85
A-14	Concentrations of Inorganic Species in Bituminous Coal Fly Ash No. 2 Leachate Generated by the CAE	86
A-15	Concentrations of Inorganic Species in Boiler Slag Leachate Generated by the ASTM-A Method	86
A-16	Concentrations of Inorganic Species in Boiler Slag Leachate Generated by the ASTM-B Method	87
A-17	Concentrations of Inorganic Species in Boiler Slag Leachate Generated by the CAE	87
A-18	Concentrations of Inorganic Species in Scrubber Sludge Leachate Generated by the ASTM-A Method	87

TABLES (continued)

Number		Page
A-19	Concentrations of Inorganic Species in Scrubber Sludge Leachate Generated by the ASTM-B Method	88
A-20	Concentrations of Inorganic Species in Scrubber Sludge Leachate Generated by the EP	88
A-21	Concentrations of Inorganic Species in Scrubber Sludge Leachate Generated by the CAE	88
A-22	Concentrations of Inorganic Species in Hopper Ash Leachate Generated by the ASTM-A Method	89
A-23	Concentrations of Inorganic Species in Hopper Ash Leachate Generated by the ASTM-B Method	89
A-24	Concentrations of Inorganic Species in Hopper Ash Leachate Generated by the EP	90
A-25	Concentrations of Inorganic Species in Hopper Ash Leachate Generated by the CAE	90
B-1	SSMS Data for the EP Leachate of Bituminous Coal Fly Ash No. 1	92
B-2	SSMS Data for the EP Leachate Blank	93

ACKNOWLEDGMENT

The authors gratefully acknowledge the guidance and support provided by the Project Officer, Mr. Frank Briden. We thank Dr. James Epler, Dr. Wayne Griest, and Dr. C.W. Francis and their co-workers at Oak Ridge National Laboratory for sharing the results obtained from their leachate investigations. The authors acknowledge the support of Dr. Kenneth Duke and his co-workers at Battelle Laboratories in Columbus, Ohio for their insight into the application of the bioassays to the leachates. The authors appreciate the cooperation provided by Ms. Cheryl Palesh at Engineering-Science, McLean, Virginia in conjunction with the ASTM round-robin program. The authors also acknowledge the following GCA/Technology Division staff members: Mr. Richard Dionne, Ms. Patrice Svetaka, Mr. Virgilio Gonzales, Ms. Mary Kozik, and Ms. Sandra Sandberg for conducting the laboratory analyses, and Ms. Susan Spinney and Ms. Jacqueline McCarthy for typing the manuscript.

SECTION 1

INTRODUCTION

The disposal of industrial wastes has become an important environmental issue. The hazardous species which could be leached from the wastes of the disposal is the primary source of concern. The magnitude of the industrial waste problem seems overwhelming. While estimates vary with their source and with the industrial categories considered, estimates of about 400 million tons have been given for annual production. Of particular interest to this study are energy processes. Electric utilities, for example, are major generators, with scrubber sludge being a growing problem. It is expected that over 30 million dry tons of scrubber sludge will be generated annually by 1985.

In order to assess the potential deleterious environmental effects that individual wastes could produce after disposal, a means of characterizing the leaching properties of waste materials is required. Characterization of the leachate from a waste material, in terms of elemental concentrations or other parameters that represent potential toxicity, is a relatively straightforward analytical exercise; however, development of a laboratory test to predict the leaching characteristics of a waste after disposal is the crux of the problem. Indeed, development of a laboratory test that attempts to accurately predict, in the general case, the fate of wastes after disposal is not a technically nor economically feasible endeavor. Individual disposal environments vary widely, and the quantities of waste requiring characterization are sufficiently large that assessment of a waste material and its disposal options using laboratory tests devised on a case-by-case basis is precluded.

The approach taken to characterizing leaching properties must then be constrained to a standard test or series of tests which can be cost effectively applied to the majority of wastes and yield information comprising a comparable set of leaching characteristics. Such data can then be used to rank the potential hazards of the waste and provide insights into the disposal requirements.

Several leachate generation methods have been suggested for the determination of the environmental impact of a landfill waste. Four generation methods were evaluated in this study. The methods studied include the Environmental Protection Agency, Office of Solid Waste (EPA-OSW) proposed procedure, the two procedures proposed by the American Society for Testing and Materials, and a procedure employing a carbon dioxide-saturated water leaching medium as an alternative to other acidic media. These evaluations were aimed at determining a single method that would be most suitable for Environmental Assessment (EA) needs.

Because the EA programs presently being conducted are principally concerned with energy systems, the leachate generation procedures investigated under this study were applied to a variety of energy process wastes. An effort was made to analyze a cross-section of these waste materials in order to determine the general applicability of the methods. Both conventional wastes and advanced process wastes were employed in the evaluations.

Also as part of this study, efforts were made to assemble and summarize the existing data on leachate procedures and to assess concurrent leachate generation studies being conducted by various organizations. These findings are presented in Sections 4 and 5 which provide an overview of the leachate generation problem and previous reports, respectively. These data are discussed in conjunction with the data resulting from this study in Section 7. All analytical data collected are tabulated in the Appendices.

SECTION 2

SUMMARY AND CONCLUSIONS

In an effort to fulfill the solid waste characterization needs of Environmental Assessment (EA) programs, four leachate generation methods have been evaluated. The evaluations include the following methods:

- EPA-OSW Extraction Procedure (EP) — an open system, acetic acid extraction.
- ASTM Method A — a closed system, water extraction.
- ASTM Method B — a closed system, acetic acid-acetate buffer extraction.
- Carbonic Acid Extraction (CAE) — a closed system CO_2-saturated water extraction.

The principal criteria used to evaluate these leachate methods were:

- General Applicability — Any procedure employed as part of EA methodology must be amenable to a wide range of waste materials.
- Reproducibility — In order to make valid judgments regarding the potential hazard of a waste, the reproducibility of the generation procedure must be well defined.
- EA Methods Compatibility — It is highly desirable that the leachate produced not necessitate modifications to the EA established analytical procedures.
- Leaching Characteristics — To the extent practical in the laboratory, the leachate generation procedure utilized should simulate the anticipated fate of the waste.

To evaluate the general applicability, the four leachate methods were applied to seven energy process wastes, including oil shale, FBC waste, fly ash, boiler slag, scrubber sludge, and hopper ash. For the wastes tested, no procedural problems were encountered with any of the leaching methods.

The final pH of the leachates generated by the ASTM-A method correlates with the predominance of iron or calcium oxide in the waste. The amorphous iron oxides produce an acidic solution, while the lime ($Ca(OH)_2$) yields a basic

extract. The basicity of the FBC waste and hopper ash offset the acidic media of the ASTM-B, EP, and CAE leachates and produced a final basic pH.

Except for mercury, the metals cited in the RCRA regulation (Ag, As, Ba, Cd, Cr, Pb, and Se) were analyzed by graphite furnace atomic absorption spectroscopy (AAS). Mercury was determined by the cold vapor method. In addition to these analyses, calcium was determined by flame AAS and the anions, fluoride, chloride, and sulfate, were quantitated by ion chromatography (IC). Graphite furnace techniques were used because the trace metal concentrations in most of the leachates were below the detection limits for flame AAS.

When the leachate concentrations are compared for the wastes extracted by all four leachate procedures, the ASTM methods produced the highest concentrations for most of the inorganic contaminants. The high leachate concentration is a reflection of the large sample quantity used for the ASTM methods (350 g) and the low liquid-to-solid ratio (4:1). The quantity of metal (or anion) leached per gram of dry solid is generally higher, however, for the EP and CAE methods. The EP, in particular, leached the largest quantities of inorganic species, which is probably an indication of its rigorous agitation method. The stainless steel extractor may also be breaking up the waste material, exposing new surfaces to the leachate, and yielding high leachate quantities which are an artifact of the shaking apparatus.

Based on the results of the extractions, it appears that some leachate procedures exhibit an elemental selectivity. More cadmium (in µg/g of dry sample) is extracted by the ASTM-B method than by the other leachate methods. The CAE leaches more of the selenium, arsenic, and silver, and the EP effectively solubilizes most of the trace elements and especially the major components, calcium and sulfate. The extraction of cadmium by the ASTM-B method seems to be correlated with the pH of the leachate. Except for the hopper ash, the cadmium was extracted in the largest quantity by the precedure having the lowest final pH. In most cases, this was the ASTM-B method.

Five of the energy wastes produced leachates which would be classified as hazardous by the RCRA criteria. The toxic leachates were extracts of oil shale, bituminous coal fly ash, scrubber sludge, and hopper ash. Hazardous leachates for the scrubber sludge and hopper ash were produced by all four methods. As indicated previously, the ASTM methods produced the highest metal concentration in the leachates, and consequently, they yielded the largest number of toxic leachates.

In most cases, the concentration of selenium exceeded the threshold level regardless of the method used for extraction. The availability of selenium on the surface of the samples and its solubility in acidic, neutral, and basic solutions account for its ease of extraction. The anionic character of selenium, probably as SeO_4^{2-}, could account for its solubility in solutions of widely varying pH.

Arsenic and chromium have also been shown to concentrate on the surface of fly ash particles and both are soluble in acidic media. Unlike selenium, however, they are sparingly soluble in H_2O. When arsenic and chromium exceeded the RCRA threshold values, it was only in the fly ash and hopper ash wastes and only for the leaching tests which used acidic solutions.

Percentages of the metals extracted from the wastes were based upon the Inductively Coupled Argon Plasma Spectroscopy (ICAPS) or AAS analysis of the total metal concentration in the waste. In general, the results indicate that less than 1 percent of the metal was leached from the wastes.

The precision of the leachate methods was determined by calculating the relative standard error (RSE) for replicate extractions of a solid waste. The ASTM methods had similar reproducibilities with the ASTM-A method ranked first. The CAE ranked third but was close to the reproducibility of the ASTM methods. The EP consistently had the poorest precision of the four leachate tests.

The compatibilities of the leachate procedures with standard EA methodologies were also evaluated in this study. The presence of the acetate ion interfered with the IC determination for fluoride and chloride. The large excesses of acetate masked the fluoride and chloride peaks and made quantitation of these anions impossible under standard operating conditions. Elimination of this interference may be possible by operating parameter modification; however, further studies would be required to address the feasibility of such resolution. Although no bioassay tests were run on the leachates generated under this program, the inherent toxicity of the EP leaching medium has been documented.[1] Since problems associated with the bioassays are apparently caused by the presence of acetate in the leachate, the ASTM-B method should also show the same effects. The leachates generated by the CAE must be subjected to the health and ecological tests to determine the compatibility of the CAE with these bioassays. The leaching media of the EP and ASTM-B methods also caused rapid deterioration of the graphite tubes during the AAS analyses. This required frequent monitoring of the condition of the graphite tubes by injection of standard solutions, resulting in decreased sample throughput and increased analytical expense.

SECTION 3

RECOMMENDATIONS

Of the four leachate procedures evaluated, the ASTM-A and Carbonic Acid Extraction would be preferred for a standard leachate test. In terms of leaching characteristics, the CAE extracts a greater quantity of inorganic contaminants than ASTM Method A. However, the reproducibility of ASTM-A is somewhat better than the CAE. No analytical problems were encountered with either method and both procedures could adequately handle the wastes tested in this program. The leachates from the CAE would have to be subjected to the bioassay tests to determine the compatibility of the CAE with the health and ecological tests.

The major criticism of all proposed procedures is the lack of sufficient detail. A standard leachate procedure must be explicitly defined in order to avoid interpretation by the analyst. As a consequence, the reliability of interlaboratory results will be enhanced; this requirement is mandatory for any standard method. For example, the agitation methods are quite susceptible to interpretation by the analyst. If the shaking apparatus and agitation rate are rigidly defined, then much of the variability in the leachate results could be eliminated. The agitation method should expose all of the waste material to the leaching medium to give an indication of the maximum quantities which would be extracted under the test conditions. It does not appear that using a reciprocating shaker, as suggested by ASTM, achieves this goal. The agitation method should also be able to leach wastes in 2-liter quantities and larger quantities as required for bio-testing.

The separation of complex, multiphase industrial wastes prior to leaching has not been adequately covered by any of the methods reviewed in this study. A separation scheme similar to that suggested by Ham[2] could be adopted. In this scheme, a series of decisions on separation is made, based on the nature of the waste. Both filtration and centrifugation are used to separate phases.

Sample preparation, or whether to use the waste in its disposed form, is another question which needs to be addressed. If the waste is to be used in its disposed form, then provisions must be made for the treatment of wastes of large masses which are not conveniently extracted in the laboratory. Should the laboratory procedure be adapted to the dimensions of the waste, or should the size of the waste be reduced (while reducing the surface area proportionally) to make it suitable for a small scale laboratory experiment?

In addition, a protocol for preserving the sample for subsequent analyses must be included in the standard leachate test. Also, the holding time of the preserved sample must be stated in the procedure. For inorganic

species, this would include acidification of the leachate prior to AAS analysis. For some ecological tests, a pH adjustment of the leachate to pH 6.5 to 8.5 may be necessary.

Finally, the objectives of the leachate test must be given primary consideration. The objectives of the test define both the type of information sought and the possible conclusions that may be reached. A test could, for example, attempt to simulate acid rain conditions, anaerobic degradation or a host of other disposal situations. The EA protocol provides for characterization of solid wastes in terms of inorganic composition. Since these data can always be used to make worst case predictions, the leachate tests should depict the more frequently encountered or typical situation; a single test cannot simulate the general case. Ostensibly this criterion suggests a low pH leaching medium.

SECTION 4

OVERVIEW OF LEACHATE PROBLEM

BACKGROUND

In an effort to predict the environmental impact of solid waste disposal, a routine leachate test is needed to characterize the leaching properties of a waste material. This concern with a waste's leaching properties adds a new dimension to environmental assessment measurement programs. Designing a leachate procedure, which can be routinely applied in the laboratory, becomes the key factor in solving this problem. The objectives of the standard leaching test should be explicitly addressed to ensure proper interpretation of the test results. The interpretation of the test results must not extend beyond the limits established by the test objectives. The experimental procedure must be described in detail to prevent interpretation by the analyst and to facilitate comparisons of interlaboratory data. Although some studies have addressed the leachate generation problem, a single procedure, which satisfies all of the needs of an Environmental Assessment (EA) Program, has not been identified. The adoption of a standard leaching test is one requirement of the Resource Conservation and Recovery Act.

A major objective of the Resource Conservation and Recovery Act of 1976 (RCRA, P.L. 94-580) is to "regulate the treatment, storage, transportation, and disposal of hazardous wastes which have adverse effects on health and the environment." Congress recognizes that a potential problem has developed with the increase of waste material discarded by the public and private sectors. Additionally, an outcome of future technological advancement may be the production of waste materials with chemical and physical characteristics not encountered previously, thus presenting subsequent disposal problems. In an effort to solve these disposal problems, RCRA also provides for the "promulgation of guidelines for solid waste collection, transport, separation, recovery, and disposal practices and systems."

The Environmental Protection Agency (EPA) has been designated to provide the above guidelines. Criteria for identifying the characteristics of the hazardous waste are to be included in these guidelines. As defined by EPA-OSW, a waste is hazardous if it meets any one of the following criteria:

- Flammable
- Corrosive
- Reactive
- Toxic

- Infectious
- Radioactive
- Contains mutagenic, carcinogenic, or teratogenic substances
- Contains substances that bioaccumulate
- Contains toxic organic substances

Identification methods to determine whether a waste meets any of the previous characteristics have been proposed by EPA. A waste is defined as toxic, hence hazardous, if the leachate concentrations of any of the contaminants listed below exceed the values in Table 1.

TABLE 1. LIST OF TOXIC SUBSTANCES

Contaminant	Concentration in Extract (mg/l)
Arsenic (As)	0.50
Barium (Ba)	10.0
Cadmium (Cd)	0.10
Chromium (Cr)	0.50
Lead (Pb)	0.50
Mercury (Hg)	0.02
Selenium (Se)	0.10
Silver (Ag)	0.50
Endrin	0.002
Lindane	0.040
Methoxychlor	1.0
Toxaphene	0.050
2,4-D	1.0
2,4,5-TP	0.10

These leachate threshold levels are equal to 10 times the EPA National Interim Primary Drinking Water Standard for these substances.

OBJECTIVES

Although the routine analysis of a leachate from a waste material can serve as a basis for defining toxicity, any effort to predict the long-term effects on the environment after disposal is extremely difficult. It would be desirable in any proposed leachate procedure to simulate the environmental conditions to which the waste will be exposed. However, any attempt to model the environmental conditions in the laboratory may be unrealistic.

Since a standard leaching method does not presently exist, the Process Measurements Branch (PMB) of EPA's Industrial Environmental Research Laboratory (IERL) at Research Triangle Park (RTP) is directing research to identify a leachate generation procedure suitable for Environmental Assessment (EA) programs. In conjunction with this effort, four leachate generation methods have been evaluated. The objective of the study was to evaluate the methods based upon the following criteria:

1. General Applicability
2. Reproducibility
3. EA Methods Compatibility
4. Leaching Characteristics

Any leachate procedure selected for environmental work must be applicable to a wide range of waste materials. With the emphasis on energy systems, the wastes being used to evaluate the procedures include those from conventional and advanced energy processes. The type of wastes leached in this project include oil shale tailings, fluidized-bed combustion waste, bituminous coal fly ash, bituminous coal boiler slag, lignitic coal scrubber sludge, and hopper ash from a coal-fired power plant. If a standard leaching test is desired, then the reproducibility of the procedure must be known to facilitate comparisons of future interlaboratory results. The reproducibility of the procedures was determined from the analyses of replicate extractions. The leachates generated by each procedure must show a compatibility with both chemical and biological EA methods. The leaching procedures are also evaluated for their leaching characteristics as an indication of the quantities extracted by each of the leachate methods.

The leachate generation procedures evaluated by GCA include:

- EPA-OSW Extraction Procedure (EP) — an acetic acid extraction
- American Society for Testing and Materials Method A (ASTM-A) — a water extraction
- American Society for Testing and Materials Method B (ASTM-B) — an acetic acid-acetate buffer extraction
- Carbonic Acid Extraction (CAE) — an extraction with CO_2-saturated water

The experimental parameters for these methods are compared in Table 2. These procedures are discussed below.

Extraction Procedure

The EP method has been proposed by the EPA-OSW to meet the RCRA guidelines in evaluating the hazards of solid waste disposal. With the addition of acetic acid to the aqueous solution, the procedure presumably intends to simulate the first stage of anaerobic degradation, involving the formation of

TABLE 2. COMPARISON OF EXPERIMENTAL PARAMETERS FOR THE ASTM-A, ASTM-B, EP, AND CAE LEACHATE METHODS

Parameter	ASTM-A	ASTM-B	EP	CAE
Leaching Medium	ASTM Type IV H_2O	Sodium Acetate Acetic acid Buffer	0.5 N acetic acid	CO_2- saturated H_2O
Minimum Sample Size	350 grams	350 grams	100 grams	100 grams
Sample Preparation	None; use in disposed form	None; use in disposed form	Grind or subject to structural integrity test	None; use in disposed form
Solid-to-liquid Ratio	1:4	1:4	1:20	1:16
Agitation Method	Reciprocating shaker recommended	Reciprocating shaker recommended	Unspecified extractor; stirring device suggested	Reciprocating shaker recommended
Agitation Time	48 hours	48 hours	24 hours	48 hours
Initial pH of Leaching Solution	5.6-5.9	4.5	5.6-5.9	3.9-4.0
Number of Extractions	1	1	1	1
Temperature	Room	Room	Room	Room

volatile, organic acids at a disposal site. The acidic medium also provides a more aggressive leaching test than the purely aqueous leachate.

The experimental procedure suggests a minimum size of 100 grams for the extraction. The separation of any liquid fraction from the original sample is accomplished by filtration or centrifugation methods. After separation, the solid portion is prepared for extraction either by grinding the solid to pass through a 9.5 mm standard sieve or by applying the structural integrity test.

After sample preparation, the solid is placed in an extractor that must be capable of thoroughly mixing the solid and the leaching medium. A stirring device is suggested, but other agitation methods may also be used. An amount of deionized water equal to 16 times the weight of sample is added. The pH of the resulting leachate is monitored, maintained at 5.0 ± 0.2 and adjusted with 0.5 N acetic acid, if necessary. The extraction proceeds for 24 hours with a maximum addition of 4 ml of acid per gram of sample permitted to maintain the pH.

After 24 hours, the mixture is filtered and deionized water is added to adjust the volume to 20 times the weight of the sample. The analysis of metals follows the flame atomic absorption methods in "Methods for Chemical Analysis of Water and Wastes," Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. (1974).

American Society for Testing and Materials Methods

ASTM has proposed two procedures to determine the leachable components of a solid waste. Both methods are "intended as a rapid means of obtaining a solution for evaluation of the extractable materials in wastes. They may be used to produce solutions for the estimation of the relative environmental hazard inherent in the leachings from the waste." Each method is intended "to determine collectively the immediate surface washing and the time-dependent, diffusion-controlled contributions to leachings from the waste." The wastes are to be used in the form in which they are disposed. Where available, sampling is to proceed using ASTM sample methods developed for the specific industry.

The water extraction (ASTM Method A) uses Type IV water for the extraction, while the ASTM Method B employs an acetic acid-acetate buffer solution to leach the metals from the wastes. The experimental procedure, however, is identical for each method. A minimum sample size of 350 grams is recommended for each method. A small portion of the sample is dried at 104 ± 2°C for 18 ± 2 hours to determine the moisture content of the sample. The quantity of sample chosen for leaching is placed in a round, wide-mouthed bottle (constructed of material appropriate for the solid waste and subsequent analyses) and mixed with the H_2O or acetate buffer. The volume, in milliliters of leachate added, is equal to four times the weight in grams of the sample. Mixing of the phases is accomplished by any apparatus that is capable of producing the constant movement equivalent to a reciprocating shaker operated at 60 to 70 1-inch cycles per minute. Agitation is continued for 48 hours, followed by vacuum filtration of the liquid phase. The leachate is to be preserved in a manner consistent with the analytical techniques. The results of the analyses are presented in milligrams leached per gram of dry sample.

Carbonic Acid Extraction

CAE was introduced as an alternative to the acidic leaching media of the previous methods. The CO_2-saturated water was intended to simulate the aggressive leaching characteristics of the acetic acid and acetate buffer solutions without having the toxicity problem associated with the bioassay tests.

In order to maintain a CO_2-saturated leachate, the extraction must be performed in a closed system. Thus, the CAE followed the basic procedure and agitation method of the ASTM methods. A minimum sample size of 100 grams is suggested for the extraction. Round, wide-mouthed linear polyethylene bottles are used to contain the leachate. The liquid-to-solid ratio is 16:1 and was chosen to minimize common ion effects, which may affect the solubility of some species in the leachate. It was also hoped that this liquid-to-solid ratio would be low enough to prevent the trace elements from being diluted below the AAS detection limits.

The carbonic acid solution is prepared by bubbling CO_2 through deionized water until the pH reaches a minimum (approximately 3.9 to 4.0). To compare variations of the procedure, the mixture was agitated at the slower rate advocated by the ASTM methods (60 cycles/minute), and at twice that rate. After shaking for 48 hours, the leachates were filtered and aliquots were removed and preserved for atomic absorption and ion chromatographic analyses.

GENERAL CONSIDERATIONS FOR LEACHATE GENERATION

An ideal leaching test should take into account the pH, buffer capacity, redox potential, temperature, ionic strength, organic constituents, and biological activity of the environment in which it is to be disposed. Since these parameters are expected to be site-specific, developing a standard leaching test to incorporate these variables is impractical and certainly could not be achieved by a single leaching procedure. These theoretical aspects of leachate generation are reviewed in a Mitre Corporation report that compares several leachate test methods.[3]

The determination of the factors that govern the release of a species from a waste has been used to define the objectives of a leaching test.[2] These factors have been identified as:

1. The highest concentration of a species found in the leachate
2. Factors controlling the above concentration
3. Total amount of a species available from a given waste
4. Rate of dissolution of a species.

A comprehensive leaching test and analysis would be needed to make these determinations. This detailed study of the leachate would certainly be very useful, but its applicability as a basis for a standard leaching test is limited. The expense (both time and monetary) of doing this type of test on a routine basis for a variety of waste materials would be prohibitive.

Contrary to the comprehensive leaching test, the standardized leaching method should be a simple, cost-effective, expedient means of assessing the hazards of solid waste disposal. The test conditions in the standardized test should be invariable and rigorously defined. This not only minimizes any "interpretation" of the procedure, but also defines the type of information yielded by the experiment. A properly designed test can provide in a short time the data needed to determine the leaching characteristics of a waste.

These short, standardized procedures can be classified as shake (or batch) tests, column tests, and field cell tests. In a shake test, the solid material and leaching solution are mixed in a container, agitated under predetermined conditions, and the liquid phase is analyzed. The shaking apparatus should be capable of exposing all of the solid waste to the leachate, without altering the physical nature of the solid. A reciprocating shaker, wrist-action shaker, rotating shaker, etc., can provide the necessary agitation. This type of test can yield data about the equilibrium concentrations of species in the leachate, and the kinetics of the process, if aliquots are withdrawn and analyzed periodically.

A column test allows the leaching medium to flow through the waste material, which is supported in a column. The design of the column test readily yields kinetic information about the leaching process, since the eluent contacts the solid for short time periods and attempts to simulate the permeability of the waste in a landfill situation. Column tests may not be compatible with the physical form of the solid waste. However, the major disadvantages of this test are the time required to acquire results, which may range from months to years, and the poor reproducibility inherent in the method, which can be caused by channeling in the column.

As scale models of actual waste disposal sites, the field cell tests are the most ambitious in mimicking environmental conditions. The test suffers the limitations that the information resulting from the test is applicable to only that site modeled, and is expensive and time-consuming.

The shake test, then, appears to fulfill the need for a short, inexpensive, standardized leaching test that can be routinely applied to a wide range of waste materials.

FACTORS AFFECTING CONCENTRATION IN LEACHATES

The concentration of a constituent in the leachate is governed by the factors listed below. Some of these parameters have been outlined previously[2] and will be reviewed briefly here. Consideration of these variables is important in the design of a standard leaching procedure.

1. Sampling and sample pretreatment
2. Composition of leaching medium
3. Solid to liquid ratio
4. Time per elution
5. Number of elutions

6. Temperature
7. Agitation method
8. Sample preservation
9. Analytical methods

Sampling and Sample Pretreatment

One of the greatest sources of variability in the leachates is caused by the composition and nature of the sample. Obtaining a homogeneous sample is difficult to achieve, and the situation is complicated by the variation in the chemical composition of the solid caused by changes in raw materials and/or plant operating conditions. These latter problems are inherent in the process and the variation in the results caused by the situation must be tolerated. However, an explicit and comprehensive sampling procedure could ensure a sample of greater homogeneity.

Treatment of the sample prior to generating the leachate can also alter subsequent results. Provision has been made in some of the proposed methods for separating solid and liquid phases and for determining the physical state in which the solid waste is to be leached. It would seem reasonable that a solid be extracted in the physical form in which it is disposed. Some leachate generation methods grind the sample or subject it to a structural integrity test (EPA-OSW method). This alteration will increase the surface area exposed to the leaching medium and artificially increase the concentrations of species in solution. A sample that has been physically changed may not give a true indication of its leaching effect upon the environment after disposal.

Composition of Leaching Medium

Probably the single most important parameter in the leaching procedure is the chemical composition of the leaching medium. Once the type of disposal or environmental conditions to be simulated by the leaching method are defined, then a suitable leaching medium can be designed to achieve this goal.

Present methods use acetic acid or acetate buffer solutions to control pH under acidic conditions and simulate anaerobic degradation, in which volatile fatty acids are produced. Extraction of the waste with distilled-deionized water uses milder leaching conditions in an effort to determine the effect of uncontaminated rainwater upon the sample. Ham, et al.,[2,4] have developed the most rigorous leaching medium to simulate an actively decomposing municipal landfill. The parameters of pH, buffering capacity, redox environment, complexing capacity, and ionic strength are incorporated into the chemical make-up of the eluent.

The leaching medium alone can determine the validity of predicting the environmental effect of a waste material after disposal. It is also the most difficult parameter to define experimentally.

Liquid-to-Solid Ratio

Since the liquid-to-solid ratio varies in a natural system, the ratio used in the laboratory must be based upon a few considerations. A high liquid-to-solid ratio will yield an increase in the number of species leached, although the concentration of each species may be lower. This reduced concentration could be an analytical problem if the result is below the detection limit. Conversely, a low ratio will increase common ion effects with only the most soluble species being leached. Detection of species may not be a problem, but the total amount of species leached may not be indicative of the natural system. Ratios range from 4:1 to 16:1 for the leaching methods examined in this project.

Time per Elution

The concentration of a substance in solution is determined not only by the liquid-to-solid ratio, but also by the time allotted for extraction. For kinetic data, the concentration can be monitored by removing aliquots of the leachate at specified periods.

Equilibrium data may be easier to obtain in a shake test, although steady-state conditions may be achieved by only a few of the species in the leachate, since the equilibrating times will differ for the various constituents. This situation is not necessarily a problem because it is unlikely that equilibrium is ever reached in a landfill situation.

In designing a leachate procedure, an elution time should be chosen which allows the system to approach a steady-state condition. The elution time should be short enough, though, to be routinely performed in the laboratory. Most of the present methods utilize an extraction period of 24 to 48 hours.

Number of Elutions

The number of times the solid is extracted can be related to the amount of material released during the leaching process. This information may give a more realistic indication of a waste's disposal behavior. Obviously, the repeated elutions require more laboratory work, and this must be justified by the additional information gained by multiple elutions. Most of the methods currently used employ only one elution of the sample.

Temperature

The temperature of the extraction affects the solubility and the rate at which substances will be released from the solid. Modeling the temperature in a landfill is difficult, since it varies with seasonal changes. Ambient laboratory temperature is usually chosen as a convenient compromise to the problem.

Agitation Method

The means of exposing the solid to the leaching solution has already been mentioned in the general description of a shake test. To reiterate, the

agitating apparatus should be capable of mixing the two phases thoroughly without altering the physical nature of the sample. If the surface area of the sample is increased during shaking, then increases in species concentration and rate of dissolution would be expected. Experimental results would have to be interpreted with respect to these developments.

A number of shaking apparati can be and have been used for the leaching procedures, including reciprocating shakers, rotating drums and a stirring device (EPA method). For a standardized procedure, the important point is to specify exactly the method of agitation to be used.

Sample Preservation

Prior to preservation of the sample, the solid and liquid phases must be separated. The method of separation could have a significant influence upon the results obtained during analysis. Filtration with a filter pore size greater than 0.45 μm allows colloidal particles (e.g., ferric hydroxide) to pass through the filter and remain suspended in the filtrate. The presence of colloidal particles could cause fluctuations in the data from atomic absorption analyses, implying a greater nonreproducibility in the method. Centrifugation of the mixture also fails to remove colloidal matter. Filtration through a pore size of 0.45 μm or less removes these colloids and bacteria and aids in achieving a filtrate of uniform composition.

Sample preservation should be an integral part of the leachate procedure. It is generally acknowledged that trace metals in solution are preserved at pH < 2 by the addition of nitric acid with storage in a linear polyethylene bottle. The amount of nitric acid required to lower the pH to 2 will vary with the buffer capacity and inherent pH of the leachate from each waste. For the EP and two ASTM procedures, sample preservation is not mentioned or is poorly defined.

For the anionic analyses by ion chromatography, the EPA recommends refrigeration at 4°C with a maximum holding time of 7 days.[5]

Analytical Methods

In a standardized leaching test, the analytical methods selected for quantitation of the toxic substances should be readily available to the average laboratory at a reasonable cost per sample. Atomic absorption has been chosen for metal analyses because of its widespread use. Atomic absorption was compared with five other instrumental methods for metal analysis,[1] including isotope dilution-spark source mass spectrometry, spark source mass spectrometry, inductively coupled plasma emission spectrometry, optical emission spectrometry, and neutron activation analysis. The results of the study indicate that AAS is comparable to the other methods for metals analysis. In performing the AAS analyses, the analyst must ensure that the data are not artifacts of interferences from the matrix. This can be determined by using the method of standard additions or by analyzing quality control samples.

SECTION 5

LITERATURE REVIEW

PREVIOUS REPORTS

This section will attempt to summarize the work on leachate methods performed prior to this project. Some of these reports deal with methods comparisons, while others discuss the results of applying those methods to solid wastes.

1. "Compilation and Evaluation of Leaching Test Methods," W. Lowenbach.[3]

   The initial portion of the report presents the theoretical considerations in selecting a leachate procedure. The theoretical aspects of thermodynamic relationships, including a dynamic model for leachate systems and kinetic considerations which include temperature, ionic strength, chemical effects, pH, buffering, organic constituents, and redox reactions as applied to leachates are addressed.

   The majority of the discussion centers on a compilation and assessment of 30 laboratory shake tests. The originator of the test is listed along with the experimental parameters covered by the test, a brief description of the procedure, and advantages and disadvantages of the test (based on the theoretical considerations), and the purpose of test, as defined by the originator.

   Three tests are recommended for further investigation:

   (a) The IUCS shake test - uses water obtained at the disposal site for the eluent with a 4:1 liquid-to-solid ratio and an agitation period of 48 hours;

   (b) Minnesota Shake Test - the waste is shaken with acetic acid buffer at a 40:1 liquid-to-solid ratio for 24 hours;

   (c) University of Wisconsin Synthetic Leachate Test - the leaching medium incorporates the theoretical parameters discussed in the report with a shaking time of 24 hours, and a 7:1 liquid-to-solid ratio.

2. "Comparison of Three Waste Leaching Tests," R.K. Ham, et al.[4]

The three tests recommended for further study in the previous report were compared in detail in this work. Associated with this study is the preliminary investigation leading to the development of the synthetic leachate test.[2] The methods comparison is also reviewed in an Executive Summary.[6]

The synthetic leachate test uses several types of leaching solutions depending upon the landfill situation to be modeled. For a stabilized municipal landfill or monolandfill, distilled, deionized water is the leaching medium. If the waste is disposed with other industrial wastes, then distilled, deionized water along with other eluents appropriate for simulating disposal site conditions is used for leachate purposes.

The composition of the synthetic leachate (Table 3) is designed to simulate the first stage of anaerobic degradation of an actively decomposing municipal landfill in which volatile organic acids and CO_2 are produced. The pH in this phase is reduced to 4.5 to 5 and modeled in the leachate by the acetate buffer. The glycine is included to demonstrate the complexing ability of organic nitrogen in the leachate. The redox potential of the leachate is controlled by the iron (II)-pyrogallol complex, with the pyrogallol also serving as an additional chelating agent. The Na^+ and SO_4^{2-} ions in the synthetic leachate aid in controlling the ionic strength of the solution.

These leaching solutions are applied to two procedures to determine the maximum release (Procedure R) of the waste or the maximum species concentration (Procedure C). Procedure R uses three elutions of the same waste material at a 1:10 solid-to-liquid ratio to estimate the maximum release of a species from the waste material. After each elution, the filtrate is removed and analyzed and fresh leachate is added. In Procedure C, the waste is removed and discarded after each of the three elutions. A portion of the leachate is removed for analysis, while the remainder is returned to leach a fresh sample of waste.

The data from the synthetic leachate test were compared with the results of the IU Conversion Systems modified 48-hour shake test (IUCS test) and the test of the Minnesota Pollution Control Agency (Minnesota test). A comparison of the test procedures is outlined in Table 4. The three tests were applied to 14 industrial wastes ranging from adhesive and paint wastes to electroplating sludge. The inorganic parameters analyzed for the comparison included Na, K, Mg, Zn, Fe,

TABLE 3. CHEMICAL COMPOSITION OF UNIVERSITY OF WISCONSIN'S SYNTHETIC MUNICIPAL LANDFILL LEACHATE

Concentration	Chemical
0.15 M	Acetic acid
0.15 M	Sodium acetate
0.050 M	Glycine
0.008 M	Pyrogallol (1,2,3-trihydroxybenzene)
0.024 M	Ferrous sulfate

Note: pH of Leachate = 4.5

TABLE 4. COMPARISON OF THREE LEACHING TESTS[a]

Parameter	Synthetic leachate test	IUCS test	Minnesota test
Leaching solution	Synthetic leachate, H_2O[b]	H_2O[b]	Acetate buffer, H_2O[b]
Solid-to-Liquid Ratio	1:10 (Process R) Varied (Process C)	1:4	1:40
Shaking technique	Slow tumbling at 3 rpm	Back and forth shaking	1 min. shake, 24 hour rest
Time per elution	24 hours	48 hours	24 hours
Number of elutions	3 or more	5	1
Temperature	Room	Room	Room

[a]From Reference 4.

[b]Distilled, deionized water.

Cu, Pb, Cd, and Cr. The selection of trace metals to be analyzed was based upon the nature of the particular waste. Determination of COD in each leachate gave an indication of the quantity of organic matter present. Some leachates were analyzed by GC-MS for specific organic compounds. The pH and conductivity of each leachate were also measured.

The analyses (Table 5) revealed that the design of the synthetic leachate test (including both the synthetic leachate and H_2O) yielded the highest concentrations and highest release of inorganic parameters among the tests. In comparing the leaching media, the synthetic leachate was the most aggressive for extracting the metals from the wastes. The synthetic leachate gave the highest concentration 74 percent of the time (52 percent for Procedure C and 22 percent for Procedure R) for parameters measured in both acidic and H_2O leachates. As might be expected, the acidic solutions as a whole were more effective then H_2O for leaching the inorganic species. The acidic leachates gave the highest concentrations of inorganic species 89 percent of the time and the highest release 96 percent of the time.

The reproducibility of the synthetic leachate test was determined using nine replicates of leachates from a paint waste generated by both Procedure R and Procedure C (Table 6). The relative standard deviations were less than 15 percent for K, Mg, Pb, Fe, and Zn using Procedure R (maximum release). However, standard deviations were generally higher for the same metals from Procedure C (maximum concentration). The variation in the Zn and Fe data was especially high. No explanation was given for the Zn results, but the Fe data indicated that Fe was precipitating out of solution with successive elutions.

One of the problems in applying the synthetic leachate to the Environmental Assessment Program is the toxicity of the leaching medium to bioassay tests. Another limitation for its use as a standard leaching test is the care required by the analyst to handle the leachate. The iron-pyrogallol complex is air sensitive and could oxidize and form a precipitate if exposed to air during the procedure. To avoid this, containers should be purged with N_2 and filtering should be done in a dry box under a nitrogen atmosphere. If these precautions are not taken, the precipitation of the Fe-pyrogallol complex could cause the coprecipitation and adsorption of some species in solution. A nonaerobic leachate has been developed by the same researchers to avoid this problem, but it contains no ferrous sulfate and does not model the redox capacity of the landfill. It also contains the acetate buffer and thus retains its toxicity to bioassay tests.

TABLE 5. THE NUMBER OF TIMES ACID OR H_2O LEACHING SOLUTIONS GAVE HIGHEST CONCENTRATIONS OR RELEASE OF AN INORGANIC PARAMETER FROM A WASTE[a]
(Only for Parameters Measured in Both Acid and H_2O Leachates)

	SLT		Minn.		IUCS	Total		
	Acid(SL)	H_2O	Acid	H_2O	H_2O	Acid	H_2O	Total tests
	Number of Times Giving Maximum Concentration							
K	10	1			1	10	2	12
Mg	8	1	1			9	1	10
Zn	11		2			13	0	13
Pb	2		4			6	0	6
Cu	2	1			1	2	2	4
Cd	1					1	0	1
						41	5	46[b]
					Total, %	89	11	
	Number of Times Giving Maximum Release							
K	8		4			12	0	12
Mg	8	1	2			10	1	11
Zn	8		4			12	0	12
Pb	1		5			6	0	6
Cu	1		2		1	3	1	4
Cd	2		1			3	0	3
						46	2	48[b]
					Total, %	96	4	

[a]From Reference 4.

[b]Totals are not equal because two tests may both give the maximum concentration but have different maximum releases. In cases where the maximum concentration or release were the same, the results were not tabulated.

TABLE 6. STANDARD DEVIATION CALCULATIONS FOR MULTIPLE REPLICATES OF PAINT WASTE LEACHED WITH SYNTHETIC LEACHATE USING SLT PROCEDURES[a]

Parameter	Day	Procedure R (N = 9) Mean value	σ	%	Procedure C (N = 9) Mean value	σ	%	Both procedures Day 1[b] Mean value	σ	%
K	1	3.86	0.16	4.1	4.00	0.17	4.3	3.93	0.17	4.7
	2	2.10	0.22	10.7	6.49	1.84	28.3			
	3	1.58	0.18	11.6	10.50	0.49	4.7			
Mg	1	9.9	0.87	8.8	8.6	0.69	8.1	9.3	1.1	11.9
	2	1.4	0.07	4.9	16.3	2.3	14.0			
	3	0.51	0.03	6.1	33.	7.5	22.7			
Zn	1	16.92	1.31	7.74	22.68	10.33	45.6	19.4	7.8	40.
	2	3.40	0.23	6.8	70.5	22.5	31.9			
	3	1.44	0.08	5.4	123.	51.	41.3			
Pb	1	0.52	0.02	4.4	0.50	0.03	6.0	0.51	0.025	5.0
	2	0.27	0.02	8.2	0.93	0.14	15.4			
	3	0.22	0.04	17.2	1.32	0.18	13.8			
Cu	1	b.d.[c]			b.d.					
	2	b.d.			b.d.					
	3	b.d.			0.32	0.09	28.3			
Fe	1	1180.	87.	7.4	1123.	71.	6.4	1152.	80.	7.0
	2	1166.	80.	7.0	904.	146.	16.3			
	3	1094.	58.	5.6	585.	204.	35.			

[a] From Reference 4.

[b] On Day 1, procedures C and R are the same.

[c] b.d. = below detection.

Several significant results obtained during the course of the Wisconsin investigation are highlighted below:

(a) A widely-applicable liquid-solid separation scheme was developed. Anything that will not filter through a 0.45 μm filter or separate during centrifugation is considered a solid and is used in the leaching test.

(b) Five agitation methods, including continuous shaking with a Gyrotory shaker, stirring with a mechanical paddle, intermittent shaking by hand, swing type shaking, or using a rotating disk shaker, were tested and results indicated that all methods provided nearly equal release.

(c) For the same wastes, cumulative release varies for times 24 hours or more, indicating that the effect of reaction time for periods greater than 24 hours is not consistent. Systems do not appear to reach equilibrium within a 24- to 72-hour period.

(d) For some wastes, multiple elutions indicate that steady-state conditions may continue over a very long time period.

(e) The amount leached from fly ash after 18 elutions ranged from 0.07 to 7 percent for Na and Fe, respectively, compared to the amount obtained by total digestion of the fly ash.

(f) Agents added to inhibit bacterial action (Ag, NO_3, Thymol, and $CuSO_4$) exhibited no consistent effect on the test results. For the wastes tested, bacterial action had little effect on the leaching characteristics within the time frame of the test.

3. "Trace Element Characterization of Coal Wastes - Second Annual Progress Report," E.M. Wewerka, et al.[7]

High sulfur coal cleaning wastes from the Illinois Basin were subjected to leaching tests to determine the trace element levels in the drainage from the coal refuse dumps. The coal refuse samples were composed of clay minerals, quartz, pyrite, and marcasite.

The shake tests, with distilled water for the leachate, revealed that the amount of dissolved solids increases as the pH of the leachate decreases. The pH of the

leachates is largely determined by the oxidation of pyrite and marcasite in the samples.

$$FeS_2 + 4O_2 + H_2 \rightarrow FeSO_4 + H_2SO_4$$

High percentages of iron, calcium, manganese, cobalt, nickel, zinc, and cadmium were leached from the refuse samples under all of the experimental conditions used. Thermodynamically, all of these elements (except calcium) have a tendency to exist as sulfides in the samples.

It was also observed that changes in surface area of the refuse produce little change in the leaching characteristics of the sample. This is indicative of a heterogeneous reaction, whose rate is controlled by a diffusion process. Thus, the rate of acid formation and solids dissolution would be determined by the movement of reactants to the sample surface or products away from the surface.

The coal refuse samples were also subjected to column leaching studies using distilled water for the leachate. The data from these tests show that the greatest release of trace elements occurs during the early contact of the leachate with the solid. Several elements, such as cobalt, nickel, cadmium, manganese, and zinc were rapidly leached from the refuse and were classified as "environmentally active." A second column test used discontinuous flow of the solution through the solid. This experiment was designed to simulate the intermittent contact of some dumps with surface or ground waters.

When the leachate flow is halted and the material is allowed to dry out, the refuse material is regenerated and, when leaching is resumed, large amounts of acid and dissolved salts are released again. This implies that disposal areas, which experience seasonal variations in precipitation, may contaminate the environment to a greater extent than a disposal site in constant contact with water.

4. "Toxicity of Leachates, Interim Progress Report," (April 1, 1978 to January 1, 1979), J.L. Epler, et al.[1]

Personnel at Oak Ridge National Laboratory have extracted several wastes (fly ash, scrubber sludge, bottom ash, and soybean process cake) using the Extraction Procedure recommended by EPA. The extracts were subjected to various bioassays to evaluate their toxicity. The effect of the acetic acid medium upon the bioassay tests was also investigated.

During the course of the project, the analysis of trace metals by AAS was compared with five other instrumental methods, including isotope dilution-spark source mass spectrometry (ID-SSMS), inductively coupled argon plasma emission spectrometry (ICAPS), optical emission spectrometry (OES), and neutron activation analysis (NAA). The data for these methods are compared in Table 7. As indicated in Table 7, the AAS data compared favorably with the results of the other methods. Since AAS instrumentation is available in most laboratories, it was recommended as the method to quantitate the trace metals in the extracts.

The results of the inorganic analyses for the EP leachates are presented in Table 8. The results for an arsenic-contaminated groundwater sample are included in the table. The arsenic-contaminated groundwater sample would be considered toxic, based on the RCRA criteria. The arsenic and cadmium levels exceed the level of 10 times the EPA Primary Drinking Water Standard allowed for each element. The cadmium value for the fly ash leachate equals the threshold level, and this extract could be labeled toxic.

The effects of the extracts on the bioassay tests was difficult to determine because of the low concentrations of organic constituents. Methods for concentrating and separating the organics present in the extracts were investigated. Solvent extraction with methylene chloride or cyclohexane was compared with concentration by XAD-2 resin. Methylene chloride proved to be the most effective solvent for concentrating and extracting the organic species from the EP extract, but methylene chloride may cause problems with the bioassays. The use of XAD-2 was selected as the most cost-effective means of preparing the organic concentrates, since the extraction of several leachates can be conducted simultaneously with a peristaltic pump.

After concentrating the organic components, the nonpolar compounds are separated from polar species by column chromatography using Florisil. The nonpolar compounds are separated further on alumina into a monoaromatic fraction, a diaromatic fraction, a polyaromatic fraction, and a heteroaromatic fraction. These fractions can then be tested separately for their effects on the bioassay tests, and the toxicity in the leachates can be attributed to a specific class of organic compounds.

5. "Technical Aspects of the Resource Conservation and Recovery Act Upon Coal Combustion and Conversion Systems," D.W. Weeter, et al.[8]

As part of the program, the literature was surveyed for the metal concentrations found in the reactants and products

TABLE 7. COMPARISON OF METALS ANALYSES FOR SEWAGE SLUDGE EP EXTRACT[a]

Metal	Average concentration ± S.D. (mg/liter) for method[b]					
	AAS	ID-SSMS	SSMS	ICAPS	OES	NAA
Ag	0.0002 ± 0.00001	–	<0.02	<0.02	–	<0.01
As	0.03 ± 0	–	<0.02	–	–	0.08 ± 0.003
Be	0.0004 ± 0.00002	–	–	–	<0.1	
Cd	1.2 ± 0	1.1 ± 0	–	0.08 ± 0.08	–	1.03 ± 0.03
Cr	0.03 ± 0.0008	<0.2	–	<0.5	–	0.06 ± 0.006
Cu	0.7 ± 0.01	0.75 ± 0.07	–	0.7 ± 0.07	–	–
Hg	0.00003 ± 0.000001	–	–	–	–	–
Ni	3.4 ± 0.2	4.1 ± 0.27	–	3.0 ± 0.3	–	–
Pb	0.03 ± 0.003	<0.05	–	<0.1	–	–
Sb	0.10 ± 0.002	–	~0.01	–	–	0.041 ± 0.005
Se	<0.002	–	≤0.01	–	–	<0.02
Tl	0.01 ± 0.001	–	≤0.01	–	–	–
Zn	36.7 ± 0.68	39.0 ± 2.2	–	45.0 ± 4.0		55 ± 1.5

[a]From Reference 1.

[b]AAS, atomic absorption spectrophotometry; ID-SSMS, isotope dilution-spark source mass spectroscopy; ICPS, inductively coupled plasma emission spectrometry; OES, optical emission spectrometry; NAA, neutron activation analysis.

TABLE 8. TRACE ELEMENTAL ANALYSES OF As-CONTAMINATED GROUNDWATER SAMPLE, EP EXTRACTS, AND BLANK[a]

Element	Concentration (mg/liter) in					
		EP extracts of				
	As-contaminated groundwater	Fly ash	Scrubber sludge	Bottom ash	Soybean process cake	Blank
Ag	<0.01	<0.01	<0.01	<0.01	<0.01	<0.001
As	412	<0.01	0.05	<0.01	<0.01	<0.001
Ba		<0.50	<0.50	<0.50	<0.50	<0.500
Be	<0.01	0.01	<0.01	<0.01	<0.01	<0.001
Cd	0.49	0.10	0.01	<0.01	<0.01	0.001
Cr	<0.01	<0.01	0.01	<0.01	<0.01	0.001
Cu	0.01	0.05	0.02	0.01	0.07	0.004
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.001
Ni	0.94	0.66	0.14	0.02	0.02	0.013
Pb	0.12	<0.01	<0.01	<0.01	<0.01	<0.001
Sb	0.30	0.04	0.03	<0.01	<0.01	<0.002
Se	0.01	<0.01	0.03[b]	<0.01[b]	<0.01[b]	<0.001
Tl	7.72	0.02	0.01	<0.01	<0.01	<0.001
Zn	0.25	1.55	0.24[b]	0.03[b]	0.11[b]	0.283
F		8.00	3.0	<0.10	<0.10	<0.100

[a]From Reference 1.

[b]Single determination.

of coal-combustion, coal-conversion processes. Metal concentrations were tabulated for coal, ash, char, tar, ash slurries and leachates of the waste products. The energy processes included coal combustion with electrostatic precipitators, flue gas desulfurization, fluidized-bed combustion, coal gasification, and coal liquefaction.

The acceptable metal concentrations in the leachates were based on the 1962 Drinking Water Standards and the 1975 National Interim Primary Drinking Water Standards. Since most of the leachate data in the literature was generated by a distilled water extraction, the lower of the two water standards was chosen for the maximum allowable metal concentration in the leachates. It was thought that the lower value would be more appropriate for this milder extraction. The RCRA proposal uses a stronger acidic medium and the maximum acceptable metal concentration, which is 10 times the 1975 drinking water standards, reflects this more agressive leaching solution.

Table 9 reviews the leachate data for the energy wastes studied in this program. If all of the leachate data found in the literature for a specific waste exceeded the acceptable level, then that waste was considered to have a definite hazardous potential (denoted by an X in Table 9) with respect to that element. The values in parentheses indicate the dilution required to equal the drinking water criteria. If only some of the leachate data exceeds the criteria, then the waste is labeled as having a probable hazardous potential with respect to that element. For leachate data that never exceeds the criteria, the waste is classified as having no hazardous potential.

As indicated in Table 9, dry disposal of fly ash poses the greatest hazardous potential. Arsenic, cadmium, chromium, copper, and lead showed definite hazardous potentials in the leachates. Most of the wastes could be classified as having a definite hazardous potential for at least one element, and only the bottom ash leachate was classified as a probable hazardous potential for all the elements reviewed. Arsenic, cadmium, chromium, iron, lead, and manganese exceed the criteria for most of the wastes tested.

6. "Evaluation of the Procedures for Identification of Hazardous Waste," Interim Report, E.P. Meier, et al.[9]

The objectives of this ongoing study are to evaluate the sampling, extraction, and analytical procedures proposed in the RCRA regulations. The 11 sites sampled include waste streams from paint, chemical, petrochemical, and steel manufacturers. A total of 26 different wastes were obtained from these industrial facilities.

TABLE 9. HAZARDOUS POTENTIAL SUMMARY[a]

Element	Coal combustion							Coal conversion		
	Electrostatic precipitators					Flue gas desulfurization				
	Wet disposal			Dry disposal						
	Bottom ash liquid	Fly ash liquid	Combined liquid	Bottom ash leachate	Fly ash leachate	Bottom ash leachate	Fly ash leachate	Fluidized bed combustion leachate	Coal gasification ash leachate	Coal liquefaction char/tar leachate
Arsenic	0[b]	0	X[c](3)	0	X(3200)	0	0	X(5)	X(64)	
Barium	-	-	-	0		0	0			
Cadmium	-	0	-	0	X(46)	0	-	-	X(2.7)	X(2)
Chloride	-	-	-	0	-	0	0	-	-	-
Chromium	-	0	-	0	X(75)	0	0	-	0	
Copper	-	0	-	-	X(4)	-	-	-	-	
Cyanide	-	-	0		-					
Fluoride	-	-	-	0	-	0	0	-	X(2.3)	
Iron	X(A)[d]	X(700)	0	0	-	0	-	0	0	X(47)
Lead	-	0	-	0	X(61)	0	-	X(1.3)	0	X(4)
Manganese	X(7)[e]	X(6)	-	-	-	0	0	X(218)	0	0
Nitrate	-	-	-		-					
Selenium	0	X(12)								
Silver	-	-	-	-	-	-	-			
Sulfate	-	0	-	0	-	-	X(10)	0		
Zinc	-	-	-	-	0	-	-	-	-	-

[a] From Reference 8.

[b] 0 - probable hazardous potential

[c] X - definite hazardous potential

[d] (A) - taken from FGD bottom ash

[e] (7) - dilution required for mean value to equal criteria

The proposed EP is being evaluated to determine:

(a) The reproducibility of the method,

(b) Whether the procedure is sufficiently explicit for use by nonexperienced personnel,

(c) What effect various extractors have upon the final leachate data,

(d) Whether the liquid-solid separation scheme is suitable for the wastes encountered.

The EP extracts were first analyzed for arsenic, lead, cadmium, barium, and chromium by ICAP emission spectroscopy. The ICAPS was used to qualitatively survey the concentrations found in the leachates. For more quantitative results, the extracts were analyzed by flame atomic absorption spectroscopy. The ICAPS results are presented in Table 10. Pond O at Site A, which is a titanium dioxide process waste from a waste disposal facility, showed high concentrations of As, Cd, Cr, and Pb in the leachate. Other extracts from sulfonation tars (Site A, Pond 10), pesticide waste (Site C), and the filter cake (Site 6) had metal concentrations below the ICAPS detection limits.

It was observed that barium, chromium, and lead had high concentrations in the EP leachates and these elements were selected for AAS analysis. The AAS data were used to calculate the relative standard deviation (RSD) of replicate extractions and replicate determinations on the same extract (Tables 11 and 12).

For much of the AAS data, the RSD is not available because the elemental concentrations were lower than the flame AAS detection limits. The relative standard deviation is less than 5 percent for both chromium and lead. However, the barium results indicate an RSD of less than 17 percent (Table 12). It appears from Table 11, though, that most of the barium variability is due to the analytical method.

The quality control data for the extracts spiked with barium (Table 13) indicate a low spike recovery. This seems to indicate that the matrix interferes with the barium analysis and suppresses the signal. Another problem occurred during the aspiration of the sample into the nitrous oxide flame. Beads formed on the burner head causing a fluctuation of the flame, which can lead to variation in the detector signal. The standard solutions did not show this problem, and it appears to be a matrix effect. This variability of the signal would increase the standard deviation of the barium

TABLE 10. ICAPS SCREENING ANALYSIS OF EP EXTRACTS: APPROXIMATE ELEMENTAL COMPOSITION OF EXTRACTS FROM SELECTED WASTE SAMPLES[a]

Sample (No. of Extracts Analyzed)	Approximate Concentration (mg/l)				
	As	Ba	Cd	Cr	Pb
Site A, Pond 13, Location 1 (1)	1.3	0.2	0.5	1.8	0.5
Site A, Pond O, Location 2 (15)	168	10.8	4.2	1400	168
Site A, Pond P, Location 2 (7)	0.6	14.2	<0.2	124	1.2
Site A, Pond 10, Sulfonation Tars (2)	<0.4	1.08	<0.02	<0.02	<0.25
Site B, Paint Sludge, Sampled 4-19-79 (3)	0.8	1.13	0.06	7.1	1.2
Site B, Paint Sludge, Sampled 6-13-79 (1)	0.6	18	0.02	4.1	0.25
Site C, Pesticide Waste (2)	<0.4	1.26	<0.02	<0.02	<0.25
Site D, Chromate Oxidation Paste	0.8	0.6	0.6	4.5	0.4
Site D, API Oil-Water Separator (3)	<0.4	<1.002	<0.02	3.6	<0.25
Site E, Electric Furnace Baghouse Dust (1)	1.6	0.8	<0.5	3.5	0.5
Site E, Blast Furnace Scrubber Filter Cake (1)	0.6	1.3	<0.02	0.4	7
Site E, Lime Sludge from Ammonia Still (1)	1.6	<0.002	<0.02	2.3	0.4
Site E, Mill Scale from Water Treatment Plant (1)	<0.4	<0.002	<0.02	3.1	<0.25
Site G, Filter Cake, Cl/Hg Process Stream (1)	<0.4	<0.002	<0.02	<0.02	<0.25
Site I, Chlorine Process Sludge (1)	1.8	0.07	—	0.3	0.9

[a] From Reference 9.

[b] Chemical, physical and spectral interferences were not minimized. Results are corrected for dilution. Data for Ponds O and P, Site A, represent averages from analyses of extracts from replicate samples; in some cases, extracts had to be diluted to bring values within the linear range of the instrument.

TABLE 11. AVERAGE RELATIVE STANDARD DEVIATION FOR AAS ANALYSES OF EP EXTRACTS[a]

Analysis (Sample source: Ponds O and P, Site A)	RSD (%)		
	Barium	Chromium	Lead
Differences between replicate determinations on a given EP extract	14.9	1.3	2.0
Differences between replicate extractions on a given sample of waste	11.0	1.8	3.0

[a]From Reference 9.

TABLE 12. EVALUATION OF EXTRACTION PROCEDURE (EP): AVERAGE MEANS AND STANDARD DEVIATIONS FOR AAS ANALYSES[a] OF EP EXTRACTS OF WASTES FROM PONDS O AND P, SITE A[b]

Sample extracted		Barium (mg/l)			Chromium (mg/l)			Lead (mg/l)		
		$\bar{X}$	S	RSD[c] (%)	$\bar{X}$	S	RSD (%)	$\bar{X}$	S	RSD (%)
Pond O	2A	1.65	0.17	10.3	1040	17	1.6	45.7	0.5	1.1
	2B	1.34	0.05	3.7	943	21	2.2	43.5	2.0	4.6
Pond P	2A	29.9	4.9	16.4	77.6	2.4	3.1	—	—	—
	2B	27.8	3.7	13.3	82.5	2.0	2.4	—	—	—

[a]Flame Atomic Absorption analyses performed in triplicate on each of three aliquots of sample extracts.

[b]From Reference 9.

[c]RSD = Relative Standard Deviation.

Note: n=3

TABLE 13. QUALITY CONTROL DATA: COMPARISON OF BARIUM SPIKE RECOVERY FROM SELECTED SAMPLES (MATRICES)[a]

Sample	Sample conc. (mg/l)	Spike (mg/l)	Spiked conc. (mg/l)	Spike Recovery (%)	RSD[b] (Analysis)
Site A, Pond P	3.10	2.00	4.96	93	11
Site B, Paint Sludge	1.96	2.00	3.98	101	33
Site D, Chromate Oxidation Paste	0.44	2.00	1.94	76	18
Site D, API Oil Separator	0.33	2.00	2.11	89	33
Site G, Filter Cake	0.15	2.00	1.84	84	7
Site I, Chlorine Process Sludge	0.39	2.00	2.28	94	23
Blank, Filtration Apparatus	0.10	2.00	2.10	100	1

[a]From Reference 9.

[b]Relative Standard Deviation.

analysis. No analytical problems were noticed for the chromium and lead and the percent recovery of spiked samples was very good.

One problem observed with the EP extract was the formation of a precipitate after several days, especially in leachates that had a high concentration of inorganic salts and organic matter. Even preserving the extract with acid at pH<2 did not prevent the precipitate from forming. During this precipitation process, metal species could coprecipitate with the solid being formed or they could adsorb onto the precipitate and be removed from the leachate. This problem is still being investigated.

7. "Final Report: Evaluation of Solid Waste Extraction Procedures and Various Hazard Identification Tests," R.M. Burd et al.[10]

Some of the objectives of this program were to determine the reproducibility of the EP, indicate problems encountered during the extractions, and to determine the suitability of the EP for waste materials. Seven solid waste samples were collected for the program, including coal-fired power plant fly ash, basic oxygen furnace (BOF) slag, fluid catalytic cracker (FCC) catalyst fines, petroleum refinery sludge, organic chemical production still bottoms, paint and pigment sludge, and spent grain from beer production. Only the leachates of the first four of these wastes were subjected to analysis for metals. The samples were sent to three state laboratories and six commercial laboratories for extraction by the EP. After extraction, the leachates were sent to a single laboratory for metal and organic analyses.

The estimation of EP reproducibility is presented in Table 14. The overall elemental precision is expressed in terms of the mean value ($\bar{X}$) and standard deviation (σ) for the nine extracts of each waste. For analyses that yielded "less than" values, the mean was not calculated and no precision is reported. The relative standard error (RSE) at the 95 percent level is calculated from the equation:

$$RSE = \frac{2S}{\sqrt{N}} \quad \text{(reported as \% of } \bar{X}\text{)}.$$

The analytical error reported in Table 14 is based only on sample analysis, using paired results for a number of samples (usually 26). The net EP reproducibility is calculated by subtracting the square of the analytical RSE from the square of the overall RSE and taking the square root of the result.

The net reproducibility for the EP ranged from ±9.2 percent for As in refinery sludge extract to ±63 percent for As in fly ash leachate. In all cases, the correction for the analytical error accounts for only a small change in the precision of the EP. Unfortunately, since the metal analyses

TABLE 14. EP REPRODUCIBILITY[a]

Sample	Metal	Overall precision (mean, standard deviation, RSE)	Analytical error (RSE)	Net EP reproducibility (RSE)
Fly ash	As	$\bar{X}$ = 0.227 ± 0.226, ± 66%	± 20%	± 63%
	Cd	—	—	NC[b]
	Cr	$\bar{X}$ = 0.080 ± 0.032, ± 26%	± 4.6%	± 26%
	Cu	—	—	NC
BOF Slag	Cr	—	—	NC
	Pb	$\bar{X}$ = 0.441 ± 0.107, ± 16%	± 11%	± 12%
	Ni	$\bar{X}$ = 0.134 ± 0.060, ± 30%	± 7%	± 29%
Catalyst fines	As	—	—	NC
	Pb	—	—	NC
	Ni	—	—	NC
	V	—	—	NC
Refinery sludge	As	$\bar{X}$ = 0.017 ± 0.006, ± 22%	± 20%	± 9.2%
	Cd	—	—	NC
	Cr	—	—	NC
	Pb	—	—	NC

[a]From Reference 10.

[b]NC - Not calculated; "less than" values reported for some of the leachates.

were done using flame atomic absorption (as specified in the EP) more data on the precision of the EP were not obtained because the concentrations were below the flame AAS detection limits. For example, arsenic, lead, and vanadium could not be quantitated for the leachate of catalyst fines.

SECTION 6

EXPERIMENTAL

Details of the four leachate generation procedures and the analyses of the metals and anions are provided below.

EPA-OSW EXTRACTION PROCEDURE

The extraction procedure is described in 43 FR 58956-58957.

Apparatus

The extractor used in the procedure is a stainless steel extractor and is based upon the diagram in 43 FR 58961, which is reproduced in Figure 1. Stirring was accomplished by a high torque stirrer purchased from the Fisher Scientific Company.

An Orion Research Model 701A pH meter, equipped with a combination glass electrode, was used to manually monitor the pH.

Procedure

A representative sample (minimum size 100 grams) is separated into solid and liquid phases by either the filtration or centrifugation method outlined in the Federal Register. None of the solid wastes examined for this project existed as two phases, and further separation was unnecessary. The minimum size of 100 grams was used for the EP.

The solid portion must pass through a 9.5 mm (3/8 inch) standard sieve. If the particle is too large, the material must be ground or subjected to the structural integrity procedure. For the energy wastes studied, the particle size was small enough to allow passage through a 9.5 mm sieve without grinding or subjection to the structural integrity test.

An amount of distilled, deionized water equal to 16 times the weight of solid was added to the waste.

The extraction mixture was stirred at 60 to 65 rpm and the pH maintained at 5.0 ± 0.2 through the manual addition of 0.5N acetic acid. The pH of the solution is adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH did not have to be adjusted more than 0.5 pH units. The pH adjustment is to be continued for at least 6 hours. A maximum addition of 4 ml of acid per gram of solid is allowed during the extraction. If the

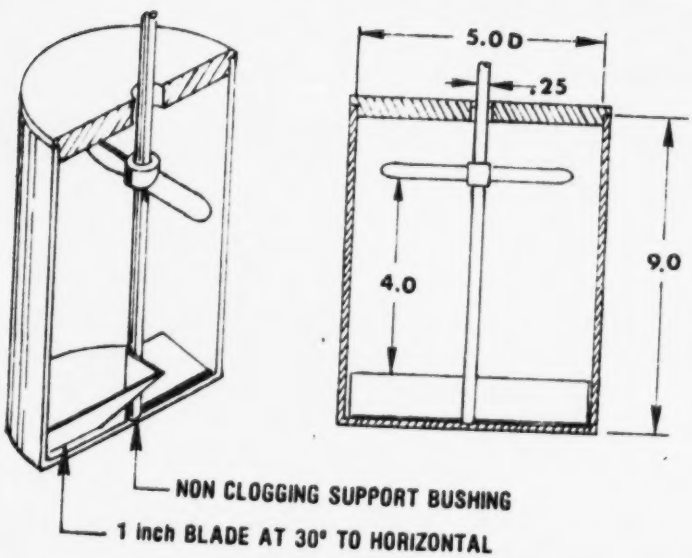


Figure 1. EP Extractor.

maximum amount of acid is added, the 24-hour extraction is completed without adding any additional acid. The temperature is maintained at 20 to 40°C during the extraction.

After 24 hours, the mixture is separated into two phases using the filtration or centrifugation methods indicated above. In this project, the extract was vacuum-filtered through a 0.45 µm Millipore filter (Type HAWP 047). The volume of the filtrate was adjusted with distilled, deionized water to 20 times the initial weight of the solid waste. Since 100 grams of material was extracted, the final volume was 2 liters.

Enough liquid was removed to completely fill an 8-ounce Nalgene LPE bottle (~275 ml) and the aliquot was refrigerated for analysis by ion chromatography. An equivalent volume was removed, acidified to pH 2 with 1:1 Ultrex nitric acid, and stored in an 8-ounce Nalgene LPE bottle for atomic absorption analysis. The remainder of the extract was stored and refrigerated in a 1-liter Nalgene LPE bottle.

ASTM-A METHOD (WATER EXTRACTION)

This water extraction procedure is currently proposed by the American Society for Testing and Materials as a method for leaching waste materials. The proposed method follows.

Apparatus

Agitation Equipment--

An Eberbach Variable-Speed Reciprocating Shaker capable of operating at 60 to 250 1-inch cycles per minute was utilized for generating the leachates. Most of the wastes were agitated at 60 cycles per minute, although a shaking rate of 120 cycles per minute was also used on some samples for comparison of the data.

Filtration--

A Millipore 0.45 µm (47 mm) membrane filter supported on a fritted glass filter separated the extract from the solid waste.

Containers--

Round, wide-mouthed, 2-liter Nalgene LPE bottles with screw tops were used for the extraction. Samples were stored in 8-ounce LPE bottles.

Procedure

Fifty grams of solid material was dried at 104 ± 2°C for 18 ± 2 hours to determine the percentage of moisture in the sample. If necessary, the drying was repeated until a constant weight was achieved.

A representative sample of waste (350.0 grams) was weighed to the nearest tenth of a gram in a 2-liter LPE bottle.

Distilled, deionized water was boiled and cooled to maintain an approximate starting pH of 6.0 (ASTM Type IV water). The quantity of water added (1400 ml) is equal to four times the weight in grams of the sample.

The container was closed and agitated continuously for 48 ± 0.5 hours at 20 ± 2°C. The samples were shaken at the rate indicated above.

After 48 hours, the aqueous phase was separated by filtering through a 0.45 µm Millipore membrane filter.

An 8-ounce LPE bottle was completely filled with the filtrate (~ 275 ml) and refrigerated for future IC analysis. Another portion of the extract was acidified to pH 2 with 1:1 Ultrex nitric acid for AAS analysis and added to an 8-ounce LPE bottle to completely fill it. The remainder of the aqueous solution was stored in a 1-liter LPE bottle and refrigerated.

ASTM-B METHOD (ACETATE BUFFER EXTRACTION)

This method is also being investigated by ASTM as a procedure for the toxic waste program. This method is proposed as an acid complement to the ASTM water extraction.

Apparatus

The equipment used for the ASTM-B procedure is identical to that described for the ASTM-A Method.

Procedure

Fifty grams of material was dried as outlined previously in the ASTM water extraction. The percentage of moisture in the sample is reported.

A representative sample of the waste (350.0 grams) was weighed to the nearest tenth of a gram and placed in a 2-liter LPE bottle.

An acetic acid-acetate buffer was prepared by dissolving 14.7 grams of glacial acetic acid and 11.1 grams of sodium acetate in 3 liters of distilled, deionized water. The pH of the buffer solution was adjusted to 4.5 ± 0.1, with the dropwise addition of acetic acid (1 M) or sodium hydroxide (1 M), as required.

The container was closed tightly and shaken at 60 1-inch cycles per minute for 48 ± 0.5 hours.

After 48 hours, the liquid phase was separated from the solid by filtering through a 0.45 µm Millipore membrane filter.

The aliquots for IC and AAS analyses were removed and treated in the manner described above for the ASTM-A Method.

CARBONIC ACID EXTRACTION

This extraction was examined as an alternative to the methods using acidic media.

Apparatus

The equipment is the same as that used for the other shaking tests (ASTM-A and ASTM-B Methods).

Procedure

A 100.0 gram portion of the sample was weighed and placed in a 2-liter LPE bottle.

Distilled, deionized water was saturated with gaseous CO_2 via a gaseous dispersion tube. A saturation period of 1 hour was required to achieve a minimum pH of 3.9 to 4.0. A 16:1 liquid-to-solid ratio was employed for the extraction and 1600 ml of CO_2-saturated water was added to the waste sample.

After adding the carbonic acid solution, the bottle was closed tightly and agitated as in the ASTM extractions for 48 ± 0.5 hours.

A 0.45 µm Millipore membrane filter separated the solid and liquid phases.

Aliquots for IC and AAS analyses were removed as described previously for the ASTM water extraction.

ATOMIC ABSORPTION

The atomic absorption analyses were done on a Perkin-Elmer Model 460 Spectrophotometer, equipped with deuterium arc background correction. Calibration curves were used to quantitate the data and determine the linear working ranges for the metals. The standard solutions were prepared in the matrix appropriate for each method. Distilled, deionized water was used in the standard solutions for the CAE Method.

All metals except Ca and Hg were analyzed by the flameless AAS technique with a Perkin-Elmer HGA-2100 Graphite Furnace. The drying, charring, and atomization cycles were optimized for each element and each matrix. Data for the standard solutions and leachate samples were recorded in the peak height mode of the instrument. Aliquot volumes of 50 or 25 µl were pipetted into the furnace with an Eppendorf pipet. For the analyses of As and Se, the solutions contained 1000 ppm Ni (as $Ni(NO_3)_2$) to minimize matrix or chemical interferences.

Since the concentration of Ca was found to be in the ppm range, Ca was analyzed in a nitrous oxide-acetylene flame, with the results recorded in the absorption mode. The ionization interferences present with the nitrous oxide-acetylene flame were controlled by the addition of a 2000 ppm potassium solution.

Mercury was analyzed using the cold vapor AAS technique. Mercury species are reduced in acidic solution with stannous chloride. The elemental mercury formed is swept through a quartz cell with nitrogen where its absorption is monitored at 253.7 nm.

For quality control purposes, EPA trace metal samples were analyzed. Some leachates for each matrix were also analyzed by the method of standard additions to ensure that no matrix interferences existed.

ION CHROMATOGRAPHY

The anionic analyses of the leachates were accomplished with a Dionex Model 14 Ion Chromatograph. The column system employed a 3 x 150 mm anion pre-column, a 3 x 250 mm anion separator column with the resin in the HCO_3^- form, and a 6 x 250 mm anion suppressor column with the resin in the H^+ form. For the F^-, Cl^-, and SO_4^{2-} determinations, a 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 solution was used as the eluent at a 30 percent flow rate. A 1 N H_2SO_4 solution regenerated the suppressor column after an 8-hour period. The injection loop had a volume of 100 µl and the sample was introduced from a 5 ml disposable syringe fitted with a Millipore filter to remove particulate matter.

SPARK SOURCE MASS SPECTROGRAPHY

Spark Source Mass Spectrography (SSMS) was used to perform a semiquantitative elemental survey analysis on the EP leachate of bituminous coal fly ash. The analysis was performed with a JEOL Analytical Instruments, Inc., Model JMS-01BM-2 Mass Spectrograph. The instrument is a high resolution, double focusing mass spectrometer with Mattauch-Herzog ion optics and ion sensitive photoplate detection.

The electrodes were prepared as follows:

- Sample aliquots (20 ml) were placed in vycor dishes and mixed with an internal standard (7.027 µg of In), approximately 200 mg of graphite, and 2 ml of distilled, deionized water.
- This mixture was slurried and dried under an infrared lamp.
- After repeating the slurrying process, the dried mixtures were placed in agate containers and further homogenized with a Spex mixer mill for 30 minutes.
- The homogeneous mixtures were then packed into polyethylene slugs and pressed into electrodes under 10 to 11 ton/in^2 pressure.

For analysis, the sample electrodes were mounted in the ion source of the mass spectrometer where they were "sparked" by a high voltage discharge which decomposed and ionized the electrode mixture. The positively charged ions were accelerated and the ion beam formed was energy focused and momentum dispersed for collection on an ion sensitive photoplate. Instrumental parameters are listed below:

- Pulse Repetition Rate (Hz) 1000
- Pulse Length (microsec) 40
- Magnet Current (A) 4.00
- Accelerating Voltage (kV) 28.4
- Analyzer Pressure (torr) 4×10^{-9}
- Source Pressure (torr) $\sim 1 \times 10^{-7}$

SECTION 7

RESULTS AND DISCUSSION

GENERAL APPLICABILITY OF THE LEACHATE METHODS

To evaluate the general applicability of the leachate methods, the four procedures were applied to a variety of energy process wastes, including oil shale, fluidized-bed combustion waste, bituminous coal fly ash, bituminous coal boiler slag, lignitic coal scrubber sludge, and hopper ash from a coal-fired power plant. Except for the hopper ash the samples were supplied by Engineering-Science as part of an ASTM interlaboratory test program to assess three extraction procedures, the ASTM-A, ASTM-B, and EP methods.[11] The program was conducted under the auspices of the American Society for Testing and Materials (ASTM) Subcommittee, D-19.12 and participating Energy Technology Centers of the U.S. Department of Energy (DOE). The data available on the samples are given in Table 15. For some of the samples, a description and analysis of the coal is included, along with the analysis of the sample itself. Most of these wastes were essentially dry, since no weight was lost when the percent moisture was determined for the ASTM methods. The only exception was the scrubber sludge, which had a weight loss of 28 percent upon drying. For the wastes tested, no procedural problems were encountered with any of the leaching methods. All of the samples were extracted in the form in which they were received. None of the wastes had to be ground or subjected to the structural integrity test, as prescribed in the EP method.

Since the samples were basically dry solids, the separation schemes of the leachate methods have not been tested thoroughly. For more complex industrial wastes, a protocol for liquid-solid separation may not be adequately addressed by some of the procedures. The EP method uses either filtration or centrifugation to separate the component phases in the original sample. The filtration procedure uses a pressurized (75 psi) system with a 0.45 μm membrane filter to separate solid and liquid phases. The filtration is stopped when no more fluid is removed from the waste. The solid and any material retained by the filter pads are combined for the extraction. For the EP centrifugation method, the sample is centrifuged for 30 minutes at 2300 rpm. The heights of the liquid and solid layers are measured to calculate the liquid-to-solid ratio. Centrifugation is repeated until the liquid-to-solid ratio is constant for two consecutive centrifugations. Either separation technique can accommodate some of the wastes that might be encountered, but a more comprehensive approach, possibly using both filtration and centrifugation, would make the EP separation scheme more effective.

TABLE 15. DESCRIPTION AND ANALYSIS OF WASTE SAMPLES[a]

1. Sample: Oil Shale

   Source: The sample was collected 1 February 1979 from the DOE's Laramie Energy Technology Center, research retort site, having been shipped there over the past two years.

   General Description:

   OS-1: Retorted (spent) oil shale from Green River Formation near Rifle, Colorado, Run No. 16; ground to pass through No. 8 mesh screen.

   Analysis:

	Total Carbon	Mineral Carbon	Organic Carbon	Nitrogen	Sulfur	Oil Yield gal/ton
OS-1:	8.86%	5.08%	3.77%	0.18%	0.45%	23.6%

2. Sample: Fluidized-Bed Combustion (FBC) Waste

   Source: FBC is from the Pope, Evans, and Robbins pilot FBC boiler in Alexandria, Virginia. The sample was obtained April 1978, directly from the boiler and stored in sealed containers at Valley Forge Laboratories in Devon, Pennsylvania.

   Approximate analysis of coal used for FBC (Western PA, Sewickley):

Carbon - 72%	Loss on Ignition - 87.8%
Sulfur - 3.8%	Ash - 12.2%

   Chemical and physical analysis of FBC by sample source:

Loss on Ignition - 7.59%	CaO - 47.19%
SiO_2 - 15.34%	MgO - 1.00%
Combined Fe & Al oxides - 7.95%	SO_4 - 19.80%
Specific gravity - 2.76%	

   Chemical analysis of FBC by receiving lab:[b]

Combined Fe and Al oxides - 1.16%
CaO - 50.23%
MgO - 0.24%

(continued)

TABLE 15 (continued)

3. Sample: Bituminous Coal Fly Ash No. 1

Source: The sample was obtained from the Keystone Station of Pennsylvania Electric Company, near Indiana, Pennsylvania. Date of sampling is unknown. Sample was provided by L. John Minnick, Consultant.

Approximate analysis of coal used for this waste:

Moisture - 3.5%

Ash - 16.75% Heat Value - 12,000 Btu/lb

Chemical and physical analysis of waste by sample source:

Loss on Ignition	- 1.40%	SiO_2	- 50.60%
Combined Fe & Al oxides	- 40.1%	CaO	- 2.2%
Moisture	- 0.3%	MgO	- 2.0%
Specific gravity	- 2.29%	SO_3	- 0.4%
Amount retained on No. 325 sieve	- 23.54%		

Chemical analysis of waste by receiving lab:

Combined Fe & Al oxides	- 22.74%
CaO	- 7.9%
MgO	- 3.19%

4. Sample: Bituminous Coal Fly Ash No. 2

Source: The sample was obtained from the Kammer Plant of Ohio Power Co., Moundsville, West Virginia, Unit No. 3. Samples were taken in February 1979 and were provided by John Faber, National Ash Association.

Approximate analysis of coal used for waste not available.

Chemical and physical analysis of waste by sample source:

No analysis was completed on the samples used in the program. A representative analysis of the fly ash is as follows:

SiO_2	- 35.5%	TiO_2	- 0.7%
Al_2O_3	- 19.4%	Calcium	- 3.1%
Fe_2O_3	- 21.6%	Magnesium	- 0.6%

(continued)

TABLE 15 (continued)

Na_2O	- 0.8%	Water loss at 110°C	- 0.8%
K_2O	- 1.7%	Net ignition loss	- 2.0%
SO_3	- 4.1%	pH of 1% slurry after 1 hour @ 24.5°C	- 4.31
Carbon	- 9.0%		

Chemical analysis of waste by receiving lab:

Al_2O_3 - 18.42%	CaO - 1.75%	Na_2O - 1.08%
Fe_2O_3 - 27.69%	MgO - 0.97%	K_2O - 1.20%
TiO_2 - 1.07%		

5. Sample: Bituminous Coal Boiler Slag

Source: The Ohio Power's Kammer Plant, as referenced for sample 4.

Approximate analysis of coal used for waste:

Moisture	- 5.46%	Fixed carbon	- 45.41%
Ash	- 14.47%	Sulfur	- 4.09%
Volatile matter	- 34.66%		

Chemical and physical analysis of waste by sample source not available.

Chemical analysis of waste by receiving lab cannot be compared to sample source results.

6. Sample: Lignite Scrubber Sludge

Source: Sample obtained from Unit No. 2 of the Milton Young Power Station (430 MW) of the Minnkota Power Cooperative, Center, North Dakota. The sample was collected on 28 February 1979, and was taken directly from the vacuum filter. The sample was provided by Oscar Manz, Coal By-Products Utilization Institute.

Approximate analysis of coal used for waste:

Moisture	- 37.1%	Fixed carbon	- 25.5%
Ash	- 9.74%	Sulfur	- 0.64%
Volatiles	- 27.66%	Btu/lb	- 6,422

(continued)

TABLE 15 (continued)

Chemical and physical analysis of waste by sample source:

SiO_2	- 18.9%	SO_4	- 26.83%
Fe_2O_3	- 3.14%	SO_2	- <0.02%
Al_2O_3	- 24.02%	Water content	- 42.38%
CaO	- 11.86%	pH	- 4.86
MgO	- 5.35%		

Chemical analysis of waste by receiving lab:

CaO	- 9.75%	Fe_2O_3	- 6.00%
Al_2O_3	- 7.37%	MgO	- 1.66%

7. Sample: Hopper Ash

Source: The sample was collected 14 February 1979 at Southwestern Public Services Harrington Station, Unit No. 2 in Amarillo, Texas.

Analyses of coal used for this waste:

Moisture	- 28.04%	Ash	- 5.51%
Volatiles	- 32.81%	Sulfur	- 0.31%
Fixed carbon	- 33.64%	Btu/lb	- 8594

Chemical analysis of Hopper Ash by GCA Laboratories:

Al_2O_3	- 13.3%	MgO	- 3.75%
CaO	- 22.9%	SiO_2	- 20.5%
Fe_2O_3	- 6.4%	TiO_2	- 1.3%
K_2O	- 0.37%		

[a] From Reference 11.

[b] Only the parameters corresponding to sample source analyses appear here. This will be true for all samples described.

The ASTM methods pay little attention to the separation of solid and liquid components in the waste. No mention is made of a preliminary separation step prior to the leaching test. For both the EP and ASTM methods, a widely applicable solid-liquid separation scheme should be included in the leachate test.

LEACHING CHARACTERISTICS

The results of the leachate tests are presented in Appendix A. The concentrations of the species in solution are given in μg per liter except for Ca, F^-, Cl^-, and SO_4^{2-}. The final pH of the leachate is given along with the volume of 0.5 N acetic acid added during the EP procedure. The final pH data are also collected and summarized in Table 16. Unless otherwise noted in Appendix A, the leachates generated by the ASTM-A, ASTM-B, or CAE methods were agitated at 60 1-inch cycles/minute.

TABLE 16. SUMMARY OF FINAL pH FOR WASTES TESTED[a]

Waste sample	ASTM-A	ASTM-B	EP	CAE
Oil shale	9.88	5.09	8.70	6.64
	11.13[b]	5.32	8.50	6.58
	10.74[c]			
	10.74[c]			
FBC waste	12.52	11.94	12.28	11.74
	12.54		12.32	
Bituminous coal Fly ash No. 1	10.4	4.5	5.0	
			5.0	
			5.0	
Bituminous coal Fly ash No. 2		3.28		3.11[d]
		3.51[d]		3.08[d]
Bituminous coal Boiler slag	3.55	4.27		4.22[d]
Lignitic coal Scrubber sludge	5.0	4.5	5.1	5.43
Hopper ash	12.13	11.03	9.44	7.30
	12.16	11.04	10.37	7.25
	12.16	11.02	10.22	7.33
Extraction blank	6.72	4.5	4.7	4.08

[a]Unless otherwise noted, the agitation rate for ASTM-A, ASTM-B and CAE was 60 cycles/minute.

[b]Sample leached with bottle lying horizontally on shaker.

[c]Sample leached with no agitation.

[d]Agitated at 120 cycles/minute.

Fly ash has been shown to affect the pH of the aquatic environment.[12] The change in pH, which may be either acidic or basic, is a function of iron and/or calcium in the fly ash. The amorphous iron oxides produce an acidic solution while the lime ($Ca(OH)_2$) yields a basic extract in distilled water. For many of the wastes, the pH of the H_2O extraction correlates with the predominance of Ca or Fe oxide (Table 16). An exception to this is the bituminous coal fly ash No. 1, which gave a basic pH in distilled water although the major oxide was iron. For the FBC waste and hopper ash, the predominance of the CaO offset the acidic media of the ASTM-B, EP, and CAE leachates and produced a final basic pH.

The release of trace metals has been correlated with the pH of the aqueous extract.[12] The desorption of trace metals from fly ash surfaces decreases with increasing pH. The extent of trace metal solubilization is determined largely by the degree of solubilization of the surface oxide associated with the trace metal. Therefore, a surface analysis of the wastes may be necessary to interpret the solubility trends of the four leachate tests. Arsenic was unique in its increased release at pH 12. If arsenic is present as an anion, as AsO_4^{3-}, it could form insoluble compounds at lower pH values (e.g., $FeAsO_4$, $K_{sp} = 1.8 \times 10^{-20}$). With an increase in pH, the free metal ions would be precipitated as hydroxides and the arsenic concentration would increase.

Some of the initial metals analyses were done by flame atomic absorption. This applies to the results for the bituminous coal fly ash No. 1 and the lignite coal scrubber sludge. Since many of the results for these leachates were below the flame AAS detection limits, it was necessary to use the graphite furnace, with its greater sensitivity, for the AAS analyses. Those metals, including all calcium data, analyzed by flame AAS are indicated in the tables in Appendix A. Arsenic and selenium were determined only by graphite furnace methods, and mercury was analyzed using the cold vapor technique. The detection limits for the AAS and IC analyses are given in Table 17.

AAS analyses were done on the leachates preserved for metals (i.e., pH adjusted to <2 with Ultrex nitric acid) and on the reserved (unpreserved) portion of the extract. Since the preservation methods for the leachates are either not defined (as in the EP) or poorly defined (as in the ASTM methods), the reserve portion of some of the leachates was analyzed to determine the effect upon the AAS results. For most of the metals, there is little difference between analyses of the preserved and unpreserved leachates. However, the time lapse between extraction and analysis may not have been sufficient to cause a loss of metals from the reserve solution. It is certainly advisable to preserve the extracts for subsequent analyses, and proper preservation methods should be explicitly defined in any standard leaching test.

The metal concentrations in the leachates, which exceeded the RCRA threshold levels, are indicated in the data tables in Appendix A. Based on the RCRA criteria, five of the energy wastes would be classified as hazardous by at least one of the leachate methods and the findings are summarized in

Table 18. The hazardous leachates were extracts of oil shale, bituminous coal fly ash, scrubber sludge, and hopper ash. Hazardous leachates for the scrubber sludge and hopper ash were produced by all four methods. In most cases, the concentration of selenium exceeded the maximum acceptable concentration of 10 times the National Interim Primary Drinking Water Standards (0.1 mg/l for Se). In the interlaboratory program conducted by Engineering-Science, selenium levels were often in excess of proposed EPA limits.[11] Arsenic, cadmium, chromium, and lead also exceeded the concentration limits in some of the leachates.

TABLE 17. DETECTION LIMITS FOR ATOMIC ABSORPTION AND ION CHROMATOGRAPHIC ANALYSES

Detection limits for atomic absorption		
Metal	Flame (ppm)	Graphite furnace (ppb)
Ag	0.06	0.5
As		1.0
Ba	0.4	1.0
Ca	0.08	
Cd	0.025	0.1
Cr	0.10	1.0
Pb	0.5	1.0
Se		5.0
Hg	1.0 ppb by cold vapor method	

Detection limits for ion chromatography	
Anion	IC (ppm)
F^-	0.1
Cl^-	0.1
SO_4^{2-}	0.2

Four toxic leachates were produced by each of the ASTM methods, while the EP and CAE methods each yielded three hazardous extracts. Presumably, the larger quantity of solid waste leached in the ASTM methods (350 grams versus 100 grams) coupled with the lower liquid-to-solid ratio employed by the ASTM procedures yields leachates with high trace metal concentrations. This would also imply that common ion effects are not a problem at this 4:1 liquid-to-solid ratio and did not limit the concentrations of some of the inorganic contaminants. The higher solution concentrations and the number of toxic extracts produced by the ASTM methods also emphasizes the subjectivity involved in deciding upon a single leachate test to determine the hazards of waste disposal. For example, it is conceivable that some metals would be

TABLE 18. WASTES CLASSIFIED AS TOXIC BY RCRA CRITERIA

Waste	Procedure	Element(s) exceeding threshold value
Oil shale	ASTM-A	Se
	ASTM-B	None[a]
	EP	None
	CAE	None
Fluidized-bed combustion waste	ASTM-A	None
	ASTM-B	None
	EP	None
	CAE	None
Bituminous coal fly ash No. 1	ASTM-A	Se
	ASTM-B	As, Se
	EP	As, Se
	CAE	NR[b]
Bituminous coal fly ash No. 2	ASTM-A	NR
	ASTM-B	As, Cr, Se
	EP	NR
	CAE	As, Cr
Bituminous coal boiler slag	ASTM-A	None
	ASTM-B	None
	EP	NR
	CAE	None
Lignitic coal scrubber sludge	ASTM-A	Se
	ASTM-B	Se
	EP	Se
	CAE	Se
Hopper ash	ASTM-A	Se
	ASTM-B	Cr, Se
	EP	Se
	CAE	Se

[a]None – no elements exceeded the threshold value.

[b]NR – not run.

leached to a greater extent (on a μg/g basis) in the EP or CAE methods, but the higher liquid-to-solid ratio could lower the concentration below the threshold level. Thus, the leachate would not be classified as hazardous and disposal of the waste would not be considered an environmental problem. To avoid this dependence upon the liquid-to-solid ratio, the criteria could be based on the micrograms of metal extracted per gram of waste.

To illustrate this point, the concentration data in Appendix A have been converted to the mass of species extracted per gram of dry sample. The general equation used to calculate the data in Tables 19 through 27 can be expressed as:

$$\text{leachate concentration} \left(\frac{\mu g}{l}\right) \times \frac{\text{leachate volume (l)}}{\text{weight of dry sample (g)}} = \frac{\mu g}{g}$$

For all wastes except the scrubber sludge, the weight of sample used in the leachate procedure was the same as the dry sample weight (either 350 or 100 grams). The scrubber sludge lost 28 percent of its weight upon drying and the dry sample weight was adjusted accordingly. The trace metals are expressed in μg/g, while calcium and the anions are reported as mg/g. The weight/weight data facilitates intermethod comparisons.

TABLE 19. COMPARISON OF LEACHATE DATA (IN μg/g)[a] FOR OIL SHALE

Species	ASTM-A	ASTM-B[b]		EP[b]		CAE[b]	
Ca (mg/g)	0.88	4.8	6.4	22	22	2.7	2.9
Ag	<0.004	<0.002	<0.002	<0.01	<0.01	0.010	0.010
As	0.44	0.26	0.23	0.24	0.32	1.4	1.3
Ba	<1.6	0.14	0.12	2.8	6.8	4.0	4.3
Cd	<0.0004	0.088	0.092	<0.002	0.006	0.006	0.003
Cr	0.019	0.12	0.072	0.28	0.19	0.022	<0.016
Hg	<0.004	<0.004	<0.004	<0.02	0.02	<0.016	<0.016
Pb	0.064	<0.004	<0.004	0.64	0.30	0.11	0.091
Se	0.17	<0.02	<0.02	<0.1	0.26	1.1	1.0
F^- (mg/g)	0.016	[c]	[c]	[c]	[c]	0.08	0.075
Cl^- (mg/g)	0.009	[c]	[c]	[c]	[c]	0.034	0.034
SO_4^{2-} (mg/g)	4.9	1.6	2.0	12.6	9.4	12.5	14.6

[a] Unless otherwise indicated, concentration given in μg/g of dry waste.

[b] Leached in duplicate.

[c] Acetate interference.

TABLE 20. COMAPRISON OF LEACHATE DATA (IN μg/g)[a] FOR FBC WASTE

Species	ASTM-A[b]		ASTM-B	EP[b]		CAE
Ca (mg/g)	3.8	4	10.8	56	56	4.3
Ag	<0.002	<0.002	<0.002	<0.01	<0.01	0.010
As	0.15	0.14	0.25	0.17	0.13	0.40
Ba	<1.6	<1.6	0.22	7.2	7.6	1.1
Cd	0.002	0.002	0.068	0.004	0.018	<0.002
Cr	0.25	0.12	0.44	0.24	0.30	0.27
Hg	<0.004	<0.004	<0.004	<0.02	0.02	<0.016
Pb	0.036	0.048	<0.004	0.16	0.21	0.093
Se	0.16	0.16	<0.02	0.24	0.24	0.45
F^- (mg/g)	0.005	0.005	[c]	[c]	[c]	0.010
Cl^- (mg/g)	0.02	0.03	[c]	[c]	[c]	0.048
SO_4^{2-} (mg/g)	3.8	4.9	2.0	17	25.6	2.6

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.

[b]Leached in duplicate.

[c]Acetate interference.

TABLE 21. COMPARISON OF LEACHATE DATA (IN μg/g)[a] FOR BITUMINOUS COAL FLY ASH NO. 1

Species	ASTM-A	ASTM-B	EP[b]		
Ca (mg/g)	0.76	1.1	2.2	3.2	3.2
Ag	<0.24	<0.24	<1.2	<1.2	<1.2
As	1.5	9.7	22.4	28.8	36.6
Ba	<1.6	<1.6	<8.0	<8.0	<8.0
Cd	<0.1	<0.1	<0.5	<0.5	<0.5
Cr	<0.4	1.2	<2.0	<2.0	<2.0
Hg	<0.004	<0.004	<0.02	<0.02	<0.02
Pb	<2.0	<2.0	<10	<10	<10
Se	0.64	0.56	2.2	2.8	0.9
F^- (mg/g)	<0.004	[c]	[c]	[c]	[c]
Cl^- (mg/g)	<0.004	[c]	[c]	[c]	[c]
SO_4^{2-} (mg/g)	1.0	1.2	3.6	4.0	4.2

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.

[b]Leached in triplicate.

[c]Acetate interference.

TABLE 22. COMPARISON OF LEACHATE DATA (IN µg/g)[a] FOR BITUMINOUS COAL BOILER SLAG

Species	ASTM-A	ASTM-B	CAE[b]
Ca (mg/g)	0.006	0.028	0.010
Ag	<0.002	<0.002	<0.008
As	<0.004	0.096	<0.016
Ba	<1.6	0.12	0.19
Cd	<0.0004	0.015	<0.002
Cr	<0.004	0.018	<0.016
Hg	<0.004	<0.004	0.019
Pb	<0.004	<0.004	<0.016
Se	<0.02	<0.02	<0.08
F^- (mg/g)	<0.004	c	<0.016
Cl^- (mg/g)	<0.004	c	0.024
SO_4^{2-} (mg/g)	0.048	0.13	0.066

[a]Unless otherwise indicated, concentration given in µg/g of dry waste.

[b]Agitated at 120 cycles/minute.

[c]Acetate interference.

TABLE 23. COMPARISON OF LEACHATE DATA (IN µg/g)[a] FOR LIGNITIC COAL SCRUBBER SLUDGE

Species	ASTM-A	ASTM-B	EP	CAE
Ca (mg/g)	3.2	3.9	14.2	13.3
Ag	<0.33	<0.33	<1.7	0.022
As	0.83	2.0	3.9	3.6
Ba	<2.2	<2.2	<11.1	1.7
Cd	<0.14	<0.14	<0.56	0.031
Cr	<0.56	<0.56	<4.0	0.027
Hg	<0.006	0.006	<0.03	<0.022
Pb	<2.8	<2.8	<14.0	0.031
Se	0.67	0.73	3.1	3.4
F^- (mg/g)	<0.006	b	b	0.049
Cl^- (mg/g)	0.012	b	b	0.087
SO_4^{2-} (mg/g)	10.9	12.6	36.4	33.6

[a]Unless otherwise indicated, concentration given in µg/g of dry waste.

[b]Acetate interference.

TABLE 24. COMPARISON OF LEACHATE DATA (IN μg/g)[a] GENERATED BY THE ASTM-A PROCEDURE FOR HOPPER ASH

Species	First replicate	Second replicate	Third replicate	Mean	Standard deviation (σ)
Ca (mg/g)	1.9	2.0	1.7	1.9	0.15
Ag	<0.002	<0.002	<0.002	<0.002	-
As	0.11	0.11	0.10	0.11	0.006
Ba	7.5	9.0	7.2	7.9	0.96
Cd	<0.0004	0.0004	<0.0004	<0.0004	-
Cr	0.48	0.48	0.44	0.47	0.023
Hg	<0.004	<0.004	<0.004	<0.004	-
Pb	0.031	0.032	0.034	0.032	0.0015
Se	1.6	2.2	1.9	1.9	0.25
F^- (mg/g)	0.038	0.039	0.039	0.039	0.00058
Cl^- (mg/g)	0.004	0.004	0.004	0.004	0
SO_4^{2-} (mg/g)	0.60	0.76	0.80	0.72	0.11

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.

TABLE 25. COMPARISON OF LEACHATE DATA (IN μg/g)[a] GENERATED BY THE ASTM-B PROCEDURE FOR HOPPER ASH

Species	First replicate	Second replicate	Third replicate	Mean	Standard deviation (σ)
Ca (mg/g)	9.2	8.8	8.8	8.9	0.23
Ag	<0.002	<0.002	<0.002	<0.002	-
As	0.28	0.28	0.24	0.27	0.023
Ba	0.48	0.52	0.52	0.51	0.023
Cd	0.027	0.020	0.028	0.025	0.004
Cr	2.2	2.0	2.0	2.1	0.12
Hg	<0.004	<0.004	<0.004	<0.004	-
Pb	<0.004	<0.004	<0.004	<0.004	-
Se	5.8	7.7	6.8	6.8	0.95
F^- (mg/g)	b	b	b	-	-
Cl^- (mg/g)	b	b	b	-	-
SO_4^{2-} (mg/g)	9.8	8.4	6.9	8.4	1.45

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.
[b]Acetate interference.

TABLE 26. COMPARISON OF LEACHATE DATA (IN μg/g)[a] GENERATED BY THE EXTRACTION PROCEDURE FOR HOPPER ASH

Species	First replicate	Second replicate	Third replicate	Mean	Standard deviation (σ)
Ca (mg/g)	44	44	44	44	0
Ag	<0.01	<0.01	<0.01	<0.01	-
As	0.30	0.60	0.34	0.41	0.16
Ba	4.2	3.6	3.4	3.7	0.42
Cd	0.01	0.002	0.002	0.005	0.0046
Cr	3.8	3.0	6.6	4.5	1.9
Hg	<0.02	<0.02	<0.02	<0.02	-
Pb	0.26	0.28	0.34	0.29	0.042
Se	4.0	3.0	3.0	3.3	0.58
F^- (mg/g)	b	b	b	-	-
Cl^- (mg/g)	b	b	b	-	-
SO_4^{2-} (mg/g)	13.4	9.0	11	11.1	2.2

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.

[b]Acetate interference.

TABLE 27. COMPARISON OF LEACHATE DATA (IN μg/g)[a] GENERATED BY THE CARBONIC ACID EXTRACTION FOR HOPPER ASH

Species	First replicate	Second replicate	Third replicate	Mean	Standard deviation (σ)
Ca (mg/g)	3.0	3.4	3.4	3.3	0.23
Ag	<0.008	<0.008	<0.008	<0.008	-
As	1.4	1.8	1.8	1.7	0.23
Ba	11.4	11.4	11.2	11.3	0.12
Cd	0.006	0.010	0.006	0.007	0.002
Cr	2.9	3.4	3.2	3.2	0.25
Hg	<0.016	<0.016	<0.016	<0.016	-
Pb	0.13	0.13	0.13	0.13	0
Se	5.6	7.5	8.0	7.0	1.3
F^- (mg/g)	0.032	0.034	0.053	0.040	0.016
Cl^- (mg/g)	0.026	0.026	0.024	0.025	0.001
SO_4^{2-} (mg/g)	4.0	4.5	4.8	4.4	0.40

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.

As indicated in Tables 19 through 27, the major components in the leachates are calcium and sulfate. The soluble trace metals exist primarily, then, as sulfates in these energy process wastes. This conclusion is supported by the findings of a previous study.[13] The IC analyses of aqueous extractions of oil-fired and coal-fired fly ashes indicated that the predominant anion in solution was SO_4^{2-}. Fourier transform infrared analysis of the water-soluble fractions supported the assumption that the soluble metals nickel, vanadium, and magnesium are sulfate forms. Cations contained in the insoluble portion of the fly ash were assumed to be oxides. An investigation of vanadium speciation in the oil-fired fly ashes revealed that the water soluble fraction contains $V^{4+}OSO_4 \cdot X\ H_2O$ with V_2O_5 in the insoluble portion of the ash.

It is also interesting to note that, regardless of the method used for extraction, selenium often exceeded the RCRA threshold value. In a study of the solubility of trace elements in coal fly ash,[14] it was determined that acidic, neutral, and basic solutions could solubilize selenium from fly ash. A 1 M HNO_3 solution was the most efficient for extracting the selenium, while the H_2O and NH_4OH extracts were comparable in the amounts leached from the fly ash, but were much lower than the acidic solution. The anionic character of selenium in the fly ash could account for its partial solubility in the H_2O extraction (ASTM-A method). Selenium is probably present as the selenate anion (SeO_4^{2-}) which is leached more readily in H_2O than a cationic species such as Cd or Cu.

As an aid to evaluating the leachate data, the number of times each leachate method gave the highest concentration or highest quantity (in mass/g of dry sample) of an inorganic contaminant is tabulated in Tables 28 and 29, respectively. The results were compared only for the four wastes extracted by all four leachate procedures. These four wastes were oil shale, FBC waste, lignite coal scrubber sludge, and hopper ash. When a waste was extracted more than once by a method, the results were averaged before comparing the data. In some cases, the results were below the detection limits of the analytical technique, and an intercomparison of the leachate tests was not made. This omission of some data sets is reflected in the number of comparisons made for each inorganic species (the maximum number of tests for each species would be four). No comparisons were made for fluoride and chloride because these anions could not be analyzed in the leachates generated by the ASTM-B and EP methods.

It is evident from Table 28 that for most of the inorganic constituents in the leachates, the ASTM methods gave the highest concentration. The ASTM methods account for the highest leachate concentration 71 percent of the time. These results are also reflected in the leachates found to be hazardous. The ASTM methods produced more toxic leachates than the other two methods. However, the quantity of metal (or anion) leached per gram of dry solid is generally higher for the EP and CAE methods. These latter methods gave the largest quantities of metal or SO_4^{2-} for many of the wastes extracted. This indicates that the maximum amount of material, whether trace or major component, has not been released from the solid during the leachate generation by the ASTM methods.

TABLE 28. NUMBER OF TIMES EACH LEACHATE TEST GAVE THE HIGHEST CONCENTRATION OF AN INORGANIC CONTAMINANT. (ONLY FOR WASTES EXTRACTED BY ALL FOUR LEACHATE METHODS.)

Contaminant	ASTM-A	ASTM-B	EP	CAE	Total comparisons
Ca		3	1		4
Ag	1			1	2
As	1	2		1	4
Ba	1				1
Cd		3			3
Cr		3			3
Hg		1	2		3
Pb	1		2		3
Se	1	1		2	4
SO_4^{2-}	2	2	—	—	4
Totals	7	15	5	4	31[a]
Percent of total comparisons	23	48	16	13	

[a]For some leachates, the concentration is below the detection limit and no comparison is made.

TABLE 29. NUMBER OF TIMES EACH LEACHATE TEST GAVE THE LARGEST QUANTITY (MASS/g OF SAMPLE) OF AN INORGANIC CONTAMINANT. (ONLY FOR WASTES EXTRACTED BY ALL FOUR LEACHATE METHODS.)

Contaminant	ASTM-A	ASTM-B	EP	CAE	Total comparisons
Ca			4		4
Ag				2	2
As			1	3	4
Ba			2	1	3
Cd		3			3
Cr		1	2		3
Hg			2		2
Pb			3		3
Se				4	4
SO_4^{2-}	—	—	3	1	4
Totals	0	4	17	11	32[a]
Percent of total comparisons	0	13	53	34	

[a]Comparisons are not made when "less than" values are reported for each leachate method.

Based on the results in Table 29, some leachate procedures exhibit an elemental selectivity. More cadmium is extracted by the ASTM-B method than by the other procedures. This trend is also observed for the extraction of selenium, arsenic, and silver by the CAE method. The EP method extracts the largest quantity of materials, especially the major components, Ca^{2+} and SO_4^{2-}. This is probably due to the higher liquid-to-solid ratio and the EP's more aggressive agitation method. However, more vigorous stirring in the EP could cause the particles to break up and expose new surfaces to the leaching medium. The results, then, might be higher for the EP, and unrealistic in predicting the environmental impact of the waste disposal.

It is difficult to explain some of the elemental selectivity indicated above. Except for the hopper ash, cadmium is preferentially extracted by the leachate solution that has the lowest pH. In most cases, this is the leachate generated by the ASTM-B method. Cadmium, which exists as a cationic species in fly ash, has been shown to be leached more readily in acidic solutions.[14]

The concentration of certain elements on the surface of fly ash may also account for some of the solubility trends. The surface predominance of an element is probably related to its volatility. The surface predominance of some trace metals has been studied by numerous instrumental surface techniques, including ion microprobe mass spectrometry, secondary ion mass spectrometry, and Auger electron spectrometry.[15] The enrichment of selenium on the surface of fly ash has been based on a volatilization-condensation concept.[16] In this concept, the selenium is volatilized during the combustion process and subsequently condenses or preferentially adsorbs onto small airborne particles that have a large surface area per unit mass. Thus, selenium may be extracted to a greater extent by the four leachate procedures than some other elements. This is evident in Table 18, where the selenium concentration often exceeded the RCRA criteria.

Arsenic and chromium are also known to concentrate on the surface of fly ash particulate. The study on trace metal solubility in coal fly ash[14] demonstrated that arsenic and chromium could be solubilized in acidic media, but they were sparingly soluble in H_2O. This information is reflected in the data for the fly ash and hopper ash samples. When the quantity of As and Cr leached by the ASTM-A method is compared with the other three methods, more As and Cr have been extracted in the acidic solutions. When arsenic and chromium exceeded the RCRA threshold values, it was only in the fly ash and hopper ash wastes and only for the leaching tests that used acidic solutions for extraction (Table 18).

The association of some trace metals with a particular surface oxide has also been investigated.[12] Most of the trace metals are associated with the iron oxides on the surface of the fly ash, but cadmium and nickel were found to exhibit a preference for the manganese portion of the fly ash coating. This preference for surface oxides is expected to influence the release of trace metals in aqueous solutions.

The association of trace metals with the major oxides is partially caused by specific interactions at the furnace temperature. It is also suggested that the distribution of trace metals in the fly ash particles is due

to its geochemical association with the various mineral forms in the coal. For example, arsenic was associated preferentially with iron on the surface of the fly ash. Arsenic probably exists in coal as an arsenical pyrite. Since the sulfides of arsenic and iron are volatile, these species could co-condense on the surface of the cooling particles.

The percentages of metals leached from the energy process wastes have been calculated in Tables 30 to 35. Except for the hopper ash, the elemental analyses were done by inductively coupled argon plasma spectrometry (ICAPS) and were supplied by Engineering-Science in conjunction with the ASTM round-robin program to evaluate leachate procedures. No ICAPS data were reported for the oil shale. Analysis of the hopper ash was conducted by the GCA Analytical Laboratory. After total digestion of the hopper ash, the metals were measured by flame AAS The results are reported in μg/g, except for Ca which is listed as percent Ca. No percentage is reported for results that were below the detection limits for either ICAPS or flameless AAS.

Many of the results indicate that less than 1 percent of the metal was leached from the waste. Chromium was extracted in a greater percentage than the other trace metals. The percentage of chromium extracted is especially high for the fly ash samples leached by the ASTM-B and CAE methods. This re-emphasizes the availability of Cr on the surface of fly ash and its solubility in acidic media. It appears that most of the other trace metals may be bound to the sample matrix in a manner that makes them unavailable for leaching. Another possibility is that the compound forms of the trace metals are not solubilized by the leaching media.

PRECISION OF LEACHATE METHODS

Another means of evaluating the four leachate procedures is to compare the precision of replicate extractions. The relative standard error (RSE) was chosen to indicate the precision of a method and is expressed as a percentage of the mean. It measures the extent to which a sample mean can be expected to fluctuate due to chance. The equation used to calculate the RSE incorporates the number of replicate extractions performed and can be expressed:

$$\text{RSE } (\%) = \frac{\sigma}{\sqrt{n}\,\bar{X}} \times 100\ \%$$

where σ is the standard deviation, n is the number of replicates, and $\bar{X}$ is the mean. The standard deviation (σ) is calculated using the equation:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N - 1}}$$

TABLE 30. PERCENTAGE LEACHED FROM THE FBC WASTE

Metal	Concentration of metal in waste[a]	ASTM-A	ASTM-B	EP	CAE
Ca	35.9%	1.1	3.0	16	1.2
Ag	<150	—	—	—	—
As	<600	—	—	—	—
Ba	80	—	0.3	9.3	1.4
Cd	<30	—	—	—	—
Cr	22	0.8	2.0	1.2	1.2
Hg	<0.0002	—	—	—	—
Pb	<450	—	—	—	—
Se	<300	—	—	—	—

[a]Results of ICAPS analysis given in µg/g unless otherwise indicated.

TABLE 31. PERCENTAGE LEACHED FROM THE BITUMINOUS COAL FLY ASH NO. 1

Metal	Concentration of metal in waste[a]	ASTM-A	ASTM-B	EP
Ca	5.65%	1.3	1.9	4.5
Ag	178	—	—	—
As	—	—	—	—
Ba	5157	—	—	—
Cd	—	—	—	—
Cr	19	—	6.3	—
Hg	0.0006	—	—	—
Pb	594	—	—	—
Se	771	0.1	0.1	0.3

[a]Results of ICAPS analysis given in µg/g unless otherwise indicated.

TABLE 32. PERCENTAGE LEACHED FROM THE BITUMINOUS COAL FLY ASH NO. 2

Metal	Concentration of metal in waste[a]	ASTM-B		CAE[b]
		First run	Second run[b]	
Ca	1.25%	19	18	51
Ag	265	0.07	0.04	0.02
As	—	—	—	—
Ba	482	0.08	0.09	0.8
Cd	—	—	—	—
Cr	312	15	15	10
Hg	0.0002	—	—	—
Pb	954	0.3	0.4	0.2
Se	1193	—	—	0.04

[a]Results of ICAPS analysis given in µg/g unless otherwise indicated.

[b]Agitated at 120 cycles/min.

TABLE 33. PERCENTAGE LEACHED FROM THE BITUMINOUS COAL BOILER SLAG

Metal	Concentration of metal in waste[a]	ASTM-A	ASTM-B	CAE[b]
Ca	0.52%	0.1	0.5	0.2
Ag	188	—	—	—
As	—	—	—	—
Ba	302	—	0.04	0.06
Cd	—	—	—	—
Cr	175	—	0.01	—
Hg	0.0003	—	—	—
Pb	629	—	—	—
Se	958	—	—	—

[a]Results of ICAPS analysis given in µg/g unless otherwise indicated.

[b]Agitated at 120 cycles/min.

TABLE 34. PERCENTAGE LEACHED FROM THE LIGNITE SCRUBBER SLUDGE

Metal	Concentration of metal in waste[a]	ASTM-A	ASTM-B	EP	CAE
Ca	6.96%	4.6	5.6	20	19
Ag	<150	—	—	—	—
As	950	0.09	0.2	0.4	0.4
Ba	4800	—	—	—	0.04
Cd	70	—	—	—	0.04
Cr	13	—	—	—	0.2
Hg	0.0003	—	—	—	—
Pb	<450	—	—	—	—
Se	<300	—	—	—	—

[a]Results of ICAPS analysis given in µg/g unless otherwise indicated.

TABLE 35. PERCENTAGE LEACHED FROM THE HOPPER ASH

Metal	Concentration of metal in waste[a]	ASTM-A	ASTM-B	EP	CAE
Ca	16.4%	1.2	5.4	27	2.0
Ag	—	—	—	—	—
As	32.9	0.3	0.8	1.2	5.2
Ba	4800	0.2	0.01	0.08	0.2
Cd	6.06	—	0.4	0.08	0.1
Cr	134	0.4	1.6	3.4	2.4
Hg	0.46	—	—	—	—
Pb	97	0.03	—	0.3	0.1
Se	—	—	—	—	—

[a]Results of AAS analysis given in µg/g unless otherwise indicated.

The relative standard error has been calculated for the replicate extractions of some wastes and is presented in Tables 36 to 40. If the RSE is compared for the hopper ash leachates (Table 36), the precision for the ASTM methods is comparable, with the ASTM-A method having slightly better reproducibility. The Carbonic Acid Extraction (CAE) is a close third in precision behind the ASTM methods. The Extraction Procedure had the worst reproducibility for the hopper ash extractions. A comparison of the precision for other wastes also indicated that the RSE for the EP was below that of the other methods. Differences in the chemical composition of the waste samples may account for some of the irreproducibility of the four extraction procedures. However, the precision of the EP was always below that of the other methods for the wastes tested.

The precision of the methods tested in this study can be compared with results of previous investigators. One study found that the intralaboratory reproducibility for the EP was quite good with chromium and lead having relative standard deviations of less than 5 percent.[9] Another investigation into the interlaboratory precision of the EP demonstrated that the relative standard error ranged from ± 9.2 percent for As in refinery sludge extract to ± 63 percent for As in fly ash leachate.[10] Eighteen laboratories participated in the round-robin program conducted by Engineering-Science and the leachate results show extreme variability for the three procedures tested (i.e., ASTM-A, ASTM-B, and EP).[11] One conclusion drawn from the data was that the precision exhibited no consistent difference between the extraction methods.

A comprehensive study was undertaken by the Electric Power Research Institute (EPRI) to evaluate the reproducibility of the proposed RCRA Extraction Procedure.[17] An analytical scheme was devised to address the following sources of variability:

1. Interlaboratory extraction variability.
2. Intralaboratory extraction variability.
3. Interlaboratory analysis variability.
4. Intralaboratory analysis variability.
5. Unallocated variability – observed variability cannot be attributed to any of the previous causes of variation.

Since the results presented in this report represent intralaboratory extraction and analysis, the intralaboratory variabilities cited in the EPRI study are highlighted. For the wastes tested and all metals except chromium, only a small portion of the variability (usually less than 10 percent) was attributed to intralaboratory extraction variability. The intralaboratory extraction variability was more than 20 percent for chromium. The intralaboratory analysis variability contributed a significant portion to the variation of the flameless AAS analyses for lead and selenium.

TABLE 36. CALCULATION OF RELATIVE STANDARD ERROR[a] FROM RESULTS OF HOPPER ASH EXTRACTIONS

	ASTM-A				ASTM-B				EP				CAE			
	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)
Ca	1.9	0.15	3	4.6	8.9	0.23	3	1.5	44	0	3	0	3.3	0.23	3	4.0
Ag	<0.002	–	3	–	<0.002	–	3	–	<0.01	–	3	–	<0.008	–	3	–
As	0.11	0.006	3	3.2	0.27	0.023	3	4.9	0.41	0.16	3	23	1.7	0.23	3	8.1
Ba	7.9	0.96	3	6.9	0.51	0.023	3	2.6	3.7	0.42	3	6.4	11.3	0.12	3	0.64
Cd	<0.0004	–	3	–	0.025	0.004	3	9.2	0.005	0.0046	3	53	0.007	0.002	3	17
Cr	0.47	0.023	3	2.8	2.1	0.12	3	3.3	4.5	1.9	3	24	3.2	0.25	3	4.5
Hg	<0.004	–	3	–	<0.004	–	3	–	<0.02	–	3	–	<0.016	–	3	–
Pb	0.032	0.0015	3	2.7	<0.004	–	3	–	0.29	0.042	3	8.1	0.13	0	3	0
Se	1.9	0.25	3	7.5	6.8	0.95	3	8.1	3.3	0.58	3	10	7.0	1.3	3	11
F^-	0.039	0.00058	3	0.9	b	–	3	–	b	–	3	–	0.04	0.016	3	23
Cl^-	0.004	0	3	0	b	–	3	–	b	–	3	–	0.025	0.001	3	2.3
SO_4^{2-}	0.72	0.11	3	8.7	8.4	1.45	3	9.8	11.1	2.2	3	12	4.4	0.40	3	5.3

[a] Relative Standard Error (RSE) (expressed as % of $\bar{X}$) $= \frac{\sigma}{\sqrt{n}\,\bar{X}} \times 100$ percent

where σ = standard deviation

$\bar{X}$ = mean

n = number of replicate extractions

[b] Acetate interference.

TABLE 37. CALCULATION OF RELATIVE STANDARD ERROR (RSE)[a] FOR EACH LEACHATE GENERATED BY THE ASTM-A METHOD

	Oil shale[b]				FBC				Hopper ash			
	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)
Ca	0.46	0.085	2	13	3.9	0.14	2	2.5	1.9	0.15	3	4.6
Ag	0.0055	0.0007	2	9.0	<0.002	–	2	–	<0.002	–	3	–
As	0.52	0.057	2	7.8	0.15	0.007	2	3.3	0.11	0.006	3	3.2
Ba	0.41	0.014	2	2.4	<1.6	–	2	–	7.9	0.96	3	6.9
Cd	0.002	0	2	0	0.002	0	2	0	<0.0004	–	3	–
Cr	0.025	0.005	2	14	0.19	0.092	2	34	0.47	0.023	3	2.8
Hg	<0.004	–	2	–	<0.004	–	2	–	<0.004	–	3	–
Pb	0.052	0	2	0	0.042	0.0085	2	14	0.032	0.0015	3	2.7
Se	0.84	0	2	0	0.16	0	2	0	1.9	0.25	3	7.5
F^-	0.012	0	2	0	0.005	0	2	0	0.039	0.00058	3	0.9
Cl^-	0.013	0.004	2	22	0.025	0.007	2	20	0.004	0	3	0
SO_4^{2-}	6.9	1.4	2	14	4.4	0.78	2	13	0.72	0.11	3	8.7

[a] $RSE = \frac{\sigma}{\sqrt{n}\,\bar{X}} \times 100$ percent.

[b] Leachate generated without agitation.

TABLE 38. CALCULATION OF RELATIVE STANDARD ERROR (RSE)[a] FOR EACH LEACHATE GENERATED BY THE ASTM-B METHOD

	Oil shale				Hopper ash			
	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)
Ca	5.6	1.13	2	14	8.9	0.23	3	1.5
Ag	<0.002	–	2	–	<0.002	–	3	–
As	0.25	0.021	2	5.9	0.27	0.023	3	4.9
Ba	0.13	0.014	2	7.6	0.51	0.023	3	2.6
Cd	0.09	0.003	2	2.4	0.025	0.004	3	9.2
Cr	0.096	0.034	2	25	2.1	0.12	3	3.3
Hg	<0.004	–	2	–	<0.004	–	3	–
Pb	<0.004	–	2	–	<0.004	–	3	–
Se	<0.02	–	2	–	6.8	0.95	3	8.1
F^-	[b]	–	2	–	[b]	–	3	–
Cl^-	[b]	–	2	–	[b]	–	3	–
SO_4^{2-}	1.8	0.28	2	11	8.4	1.45	3	9.8

[a] $RSE = \frac{\sigma}{\sqrt{n}\,\bar{X}} \times 100$ percent.

[b] Acetate interference.

TABLE 39. CALCULATION OF RELATIVE STANDARD ERROR (RSE)[a] FOR EACH LEACHATE GENERATED BY THE EP

	Oil shale				FBC waste				Bituminous coal fly ash No. 1				Hopper ash			
	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)
Ca	22	0	2	0	56	0	2	0	2.9	0.58	3	12	44	0	3	0
Ag	<0.01	–	2	–	<0.01	–	2	–	<1.2	–	3	–	<0.01	–	3	–
As	0.28	0.057	2	14	0.15	0.028	2	13	29.3	7.1	3	14	0.41	0.16	3	23
Ba	4.8	2.83	2	42	7.4	0.28	2	2.7	<8.0	–	3	–	3.7	0.42	3	6.4
Cd	<0.002	–	2	–	0.011	0.010	2	64	<0.5	–	3	–	0.005	0.0046	3	53
Cr	0.24	0.064	2	19	0.27	0.042	2	11	<2.0	–	3	–	4.5	1.9	3	24
Hg	<0.02	–	2	–	<0.02	–	2	–	<0.02	–	3	–	<0.02	–	3	–
Pb	0.47	0.24	2	36	0.19	0.035	2	13	<10	–	3	–	0.29	0.042	3	8.1
Se	<0.1	–	2	–	0.24	0	2	0	2.0	0.97	3	28	3.3	0.58	3	10
F^-	b	–	2	–	b	–	2	–	b	–	3	–	b	–	3	–
Cl^-	b	–	2	–	b	–	2	–	b	–	3	–	b	–	3	–
SO_4^{2-}	11	2.26	2	15	21.3	6.1	2	20	3.9	0.31	3	46	11.1	2.2	3	12

[a] $RSE = \frac{\sigma}{\sqrt{n}\,\bar{X}} \times 100$ percent.

[b] Acetate interference.

TABLE 40. CALCULATION OF RELATIVE STANDARD ERROR (RSE)[a] FOR EACH LEACHATE GENERATED BY THE CAE METHOD

	Oil shale				Bituminous coal fly ash No. 2				Hopper ash			
	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)	$\bar{X}$	σ	n	RSE (%)
Ca	2.8	0.14	2	3.5	6.4	0.71	2	7.8	3.3	0.23	3	4.0
Ag	0.01	0	2	0	0.04	0	2	0	<0.008	–	3	–
As	1.4	0.07	2	3.5	21	0.71	2	2.4	1.7	0.23	3	8.1
Ba	4.2	0.21	2	3.5	3.7	0.21	2	4.0	11.3	0.12	3	0.64
Cd	0.005	0.002	2	28	2.2	0	2	0	0.007	0.002	3	17
Cr	<0.016	–	2	–	32	3.5	2	7.7	3.2	0.25	3	4.5
Hg	<0.016	–	2	–	<0.016	–	2	–	<0.016	–	3	–
Pb	0.10	0.013	2	9.2	2.2	0.071	2	2.3	0.13	0	3	0
Se	1.1	0.07	2	4.5	0.52	0.021	2	2.9	7.0	1.3	3	11
F^-	0.078	0.004	2	3.6	0.17	0.021	2	8.7	0.04	0.016	3	23
Cl^-	0.034	0	2	0	0.11	0.007	2	4.5	0.025	0.001	3	2.3
SO_4^{2-}	13.6	1.5	2	7.8	45	0.71	2	1.1	4.4	0.4	3	5.3

[a] $RSE = \frac{\sigma}{\sqrt{n}\,\bar{X}} \times 100$ percent.

[b] Agitated at 120 cycles/minute.

The following conclusions can also be drawn from the EPRI study:

1. Most of the variation in the results of the As, Ba, Cd, and Pb analyses by graphite furnace and Ba and Se analysis by flame AAS could be attributed to interlaboratory analysis variability.

2. For all metals, most of the variation in the flame and furnace results was due to the analytical method.

In addition to variation in the analyses, the reduced precision of the EP may also be caused by several other factors. The EP was the only leachate test that was not done in a closed system. In the open system, conditions are not as strictly controlled and this could result in reduced precision. In the EPRI study, a significant proportion of the variation in the graphite furnace analyses of chromium and selenium was due to either interlaboratory or intralaboratory extraction variability. Another source of nonreproducibility could be the agitation method of the EP. The stirring device can grind particles on the walls and bottom of the cylinder. This reduction in particle size exposes new surfaces to be leached and is probably done in an irreproducible manner.

VARIATIONS IN LEACHATE PROCEDURES

Some of the leachate procedures were varied to determine the effect on the leachate results. For example, data are presented in Table 41 for oil shale leachate generated by altering the ASTM-A procedure. Since the agitation rate suggested by ASTM is not very vigorous, the oil shale was extracted without agitation (third and fourth run). The quantities extracted from the oil shale without shaking are comparable to the concentrations leached while shaking at 60 cycles/minute. This is an indication that the agitation rate suggested by ASTM does little to promote the exposure of the solid to the leaching solution. The solubilization of species from the waste is largely a diffusion-controlled process. In support of the slower agitation rate, it can be said that the physical size of the sample will remain intact but this could be accomplished under more vigorous conditions, too.

The oil shale was also leached by the ASTM-A method with the extraction bottle lying horizontally on the reciprocating shaker. In this position, more waste is exposed to the leachate and even the shaking rate of 60 cycles/minute creates a wave motion that aids in exposing fresh solid to the solution. This more effective mixing is evident in the analytical data (second run). For many of the inorganic species, the amount leached has nearly doubled with the bottle in a horizontal position.

The results are presented in Table 42 for extracts of bituminous coal fly ash No. 2 generated by the ASTM-B and CAE methods. The leachates of ASTM-B were generated at the normal agitation rate and at twice the rate (120 cycles/minute) with the bottle in an upright position. There is little difference in the data between the two leachates. The CAE method was conducted in duplicate at the higher shaking rate to examine the effect on precision. The reproducibility is comparable to that for the CAE method at the lower shaking rate.

TABLE 41. COMPARISON OF ANALYTICAL DATA (IN μg/g)[a] GENERATED BY VARIATIONS OF ASTM-A PROCEDURE FOR OIL SHALE

Species	First run	Second run[b]	Third run[c]	Fourth run[c]
Ca (mg/g)	0.88	1.8	0.52	0.4
Ag	<0.004	0.008	0.006	0.005
As	0.44	0.92	0.56	0.48
Ba	<1.6	0.36	0.40	0.42
Cd	<0.0004	0.002	0.002	0.002
Cr	0.019	0.048	0.028	0.021
Hg	<0.004	<0.004	<0.004	<0.004
Pb	0.064	0.096	0.052	0.052
Se	0.17	2.1	0.84	0.84
F^- (mg/g)	0.016	0.026	0.012	0.012
Cl^- (mg/g)	0.009	0.015	0.016	0.010
SO_4^{2-} (mg/g)	4.9	9.5	7.9	5.9

[a] Unless otherwise indicated, concentration in μg/g of dry waste.

[b] Leachate generated with bottle lying horizontally on shaker.

[c] Leachate was not shaken.

The combined results for the variations in the ASTM methods suggest that the means of agitation must be changed if the leachate is to be an indication of the maximum impact of the waste disposal upon the environment. It appears that merely increasing the rate of the reciprocating shaker, as has been suggested by ASTM in a recent revision to its proposed methods, will not yield a significant increase in the mixing of the solid and leaching medium. Recent data generated by ASTM have shown statistical significance when the ASTM-A was run at 180 cycles/minute vs. 60 cycles/minute.

COMPATIBILITY WITH ENVIRONMENTAL ASSESSMENT PROCEDURES

The inherent toxicity of the EP leachate to various bioassay tests has been documented by the results of the work at Oak Ridge National Laboratory.[1] The acetate ion poses problems with aquatic toxicity and phytotoxicity tests. Experiments have shown that acetate ion is phytotoxic. The chronic aquatic bioassay uses the reproduction of daphnia magna to determine the toxicity of waste extracts. It is believed that the acetate in the extracts may serve as a substrate for the bacteria. The bacteria are fed on by the daphnids causing an artificial increase in the production of young. In control experiments, the

production of young was significantly higher for acetic acid solutions than for extracts using only water. The same would be true of the buffer solution in the ASTM-B method and this problem was a source of major concern in the synthetic leachate developed by Ham at the University of Wisconsin.[4]

TABLE 42. COMPARISON OF LEACHATE DATA (IN μg/g)[a] FOR BITUMINOUS COAL FLY ASH NO. 2

Species	ASTM-B		CAE	
	First	Second[b]	First[b]	Second[b]
Ca (mg/g)	2.4	2.2	6.9	5.9
Ag	0.18	0.10	0.04	0.04
As	17	18	21	20
Ba	0.38	0.44	3.8	3.5
Cd	1.6	1.9	2.2	2.2
Cr	46	46	34	29.0
Hg	<0.004	<0.004	<0.016	0.019
Pb	2.4	3.7	2.2	2.1
Se	<0.02	<0.02	0.53	0.50
F^- (mg/g)	c	c	0.15	0.18
Cl^- (mg/g)	c	c	0.11	0.10
SO_4^{2-} (mg/g)	41	46	45	44

[a]Unless otherwise indicated, concentration given in μg/g of dry waste.

[b]Agitated at 120 cycles/minute.

[c]Acetate interference.

The acetic acid matrices of the ASTM-B and EP also caused some analytical problems. It is possible that none of these problems was observed in previous investigations because the amount of 0.5 N acetic acid added during the EP varies from one waste to another. In many of the wastes tested in this study, the maximum volume of acetic acid (400 ml) was added during the experiment. These acidic media caused rapid deterioration of the graphite tubes. Standard solutions had to be injected more frequently to monitor the condition of the graphite tubes. This resulted in increased analytical time, and, with more frequent tube replacement, increased expense. The acetic acid matrices produced some initial background problems. Analyses for lead in the leachates generated by the ASTM-B and CAE methods could be achieved only by using the deuterium background correction capabilities of the instrument.

It is also possible that the acetic acid matrix caused some of the variation in the results observed for the EP. The injection of strong acidic solutions into the graphite furnace can degrade the analytical precision. The strong acidic solutions "wet" the inner surface of the graphite tube and cause variable distribution of the injected sample. This variable distribution will reduce the precision of replicate injections. If the absorbance data are examined for the injections of the EP leachates, it is apparent that the reproducibility has been degraded for replicate injections. However, the reduced analytical precision for the EP does not sufficiently account for the differences in precision between the EP and the other three leachate tests.

The acetate ion in the ASTM-B and EP solutions interfered with the determination of fluoride and chloride in the IC analyses. The retention time of the acetate ion is comparable to the retention times of the fluoride and chloride ions and its presence in large excess masked the determination of the fluoride and chloride concentrations.

No problems were encountered during the analysis of the leachates generated by the ASTM-A or CAE methods. The presence of carbonic acid is effectively suppressed during the IC analysis.

Since SSMS is utilized in EA programs for the elemental analysis of various environmental samples, the compatibility of the leachate with SSMS analysis was investigated. SSMS data for the EP leachate of bituminous coal fly ash No. 1 and the EP leachate blank are presented in Appendix B. The EP leachate of the fly ash posed no problems during the electrode preparation and subsequent SSMS analysis. Although no SSMS data are reported in this study for leachates generated by the ASTM-A method, SSMS analyses of ASTM-A leachates generated previously in our laboratory have not indicated any analytical problems.

It can be argued that the analytical problems indicated in this study would not be encountered in the proposed RCRA analytical scheme. Since AAS analyses are to be done by flame techniques, the problems associated with the graphite furnace would not exist. In addition, it is not necessary to determine the exact concentration of the metal in the leachate, but just show that its concentration is below the proposed threshold level. To do this, flame AAS would be sufficient. Since IC analyses of the anions is not specified in the RCRA procedures, the acetate problem associated with the IC is not important either.

However, it is possible that in the future the RCRA criteria could become more stringent and the maximum allowable concentrations would be reduced. This reduction in the threshold level might necessitate the use of the graphite furnace to quantitate the metals in the leachate. If this were to happen, the problems cited above would become relevant to the selection of a standard leachate test.

REFERENCES

1. Epler, J.L., W.H. Griest, M.R. Guerin, M.P. Maskarinec, D.A. Brown N.T. Edwards, C.W. Gehrs, B.R. Parkhurst, B.M. Ross-Todd, D.S. Shriner, H.W. Wilson, F.W. Larimer, and T.K. Rao. Toxicity of Leachates. Interim Progress Report. April 1, 1978 to January 1, 1979. Oak Ridge National Laboratory, Oak Ridge, Tennessee. Prepared for Office of Solid Waste and U.S. Environmental Protection Agency. EPA-IAG-78-D-X0372. 121 pp.

2. Ham, R., M.A. Anderson, R. Stegmann, and R. Stanforth. Background Study on the Development of a Standard Leaching Test. EPA-600/2-79-109. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1979. 249 pp.

3. Lowenbach, W. Compilation and Evaluation of Leaching Test Methods. EPA-600/2-78-095. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1978. 102 pp.

4. Ham, R.K., M.A. Anderson, R. Stegmann, and R. Stanforth. Comparison of Three Waste Leaching Tests. EPA-600/2-79-071. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1979. 214 pp.

5. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1979. 430 pp.

6. Ham, R.K., M.A. Anderson, R. Stegmann, and R. Stanforth. Comparison of Three Waste Leaching Tests, Executive Summary. EPA-600/8-79-001. U.S. Environmental Protection Agency, Cincinnati, Ohio. 1979. 24 pp.

7. Wewerka, E.M., J.M. Williams, N.E. Vanderborgh, A.W. Harmon, P. Wagner, P.L. Wanek, and J.D. Olsen. Trace Element Characterization of Coal Wastes — Second Annual Progress Report. EPA-600/7-78-028a. U.S. Environmental Protection Agency, Washington, D.C. 1978. 144 pp.

8. Weeter, D.W., and M.P. Bahor. Technical Aspects of the Resource Conservation and Recovery Act Upon Coal Combustion and Conversion Systems. Department of Civil Engineering, University of Tennessee, Knoxville, Tennessee. Prepared for Office of Environmental Policy Analysis, Oak Ridge National Laboratory, Oak Ridge, Tennessee. ORNL/OEPA-10. 1979. 73 pp.

9. Meier, E.P., L.R. Williams, R.G. Seals, L.E. Holboke, and D.C. Hemphill. Evaluation of the Procedures for Identification of Hazardous Waste, Interim Report, August 1979. EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 1979. 43 pp.

10. Burd, R.M., and J.M. Riddle. Evaluation of Solid Waste Extraction Procedures and Various Hazard Identification Tests. Cyrus Wm. Rice Division, NUS Corporation, Pittsburgh, Pennsylvania. EPA Contract No. 68-01-4725. 1979. 85 pp.

11. American Society for Testing and Materials, interlaboratory evaluation of EP and ASTM Methods. Report submitted for publication 1979.

12. Theis, T.L., and J.L. Wirth. Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems. Environmental Science and Technology, 11, 1096-1100. 1977.

13. Henry, W.M. Methods for Analyzing Inorganic Compounds in Particles Emitted from Stationary Sources, Interim Report. EPA-600/7-79-206. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1979. 122 pp.

14. Dreesen, D.R., L.I. Wangen, E.S. Gladney, and J.W. Owens. Solubility of Trace Elements in Coal Fly Ash. In: Environmental Chemistry and Cycling Processes, proceedings of a symposium held at Augusta, Georgia. 1976. pp. 240-252.

15. Linton, R.W., A. Loh, D.F.S. Natusch, C.A. Evans, Jr., and P. Williams. Surface Predominance of Trace Elements in Airborne Particles. Science, 191, 852-854. 1976.

16. Natusch, D.F.S., J.R. Wallace, and C.A. Evans, Jr. Toxic Trace Elements: Preferential Concentration in Respirable Particles. Science, 183, 202-204. 1974.

17. Electric Power Research Institute. Proposed RCRA Extraction Procedure: Reproducibility and Sensitivity. Palo Alto, California. 27 pp.

APPENDIX A

TABLES OF LEACHATE CONCENTRATIONS OF INORGANIC CONTAMINANTS (UNLESS OTHERWISE INDICATED IN THE TABLES, THE CONCENTRATIONS ARE GIVEN IN μg/l)

TABLE A-1. CONCENTRATIONS OF INORGANIC SPECIES IN OIL SHALE LEACHATE GENERATED BY THE ASTM-A METHOD[a]

Species	Preserved	Reserve
Ca (mg/l)[b]	220	220
Ag	1.0	1.6
As	110	83
Ba[b]	<400	<400
Cd	<0.1	<0.1
Cr	4.7	5.5
Hg	<1.0	<1.0
Pb	16	18
Se	41	41
F^- (mg/l)	3.9	
Cl^- (mg/l)	2.3	
SO_4^{2-} (mg/l)	1230	

[a]Final pH: 9.88.

[b]Analyzed by flame AAS.

TABLE A-2. CONCENTRATIONS OF INORGANIC SPECIES IN OIL SHALE LEACHATE GENERATED BY VARIATIONS OF THE ASTM-A METHOD

	First run[a]	Second run[b]	Third run[b]
Final pH	11.13	10.74	10.74
Species			
Ca[c] (mg/1)	460	130	100
Ag	2.0	1.5	1.3
As	230	140	120
Ba	90	100	105
Cd	0.6	0.4	0.4
Cr	12.0	7.1	5.2
Hg	<1.0	<1.0	<1.0
Pb	24	13.0	13.0
Se (µg/1)	530[d]	210[d]	210[d]
F^- (mg/1)	6.6	2.9	3.0
Cl^- (mg/1)	3.8	3.9	2.4
SO_4^{2-} (mg/1)	2370	1960	1480

[a] 2L LPE Bottle placed horizontally on shaker.

[b] Leaching mixtures were not shaken.

[c] Analyzed by flame AAS.

[d] Exceeds RCRA criteria.

TABLE A-3. CONCENTRATIONS OF INORGANIC SPECIES IN OIL SHALE LEACHATE GENERATED BY THE ASTM-B METHOD

	First replicate	Second replicate
Final pH	5.09	5.32
Species		
Ca (mg/1)[a]	1200	1600
Ag	<0.5	<0.5
As	64	58
Ba	34	31
Cd	22	23
Cr	31	18
Hg	<1.0	<1.0
Pb	<1.0	<1.0
Se	<5.0	<5.0
F^- (mg/1)	Acetate interference	
Cl^- (mg/1)	Acetate interference	
SO_4^{2-} (mg/1)	400	510

[a] Analyzed by flame AAS.

TABLE A-4. CONCENTRATIONS OF INORGANIC SPECIES IN OIL SHALE LEACHATE GENERATED BY THE EP

	First replicate	Second replicate
Initial pH	10.7	10.8
Final pH	8.7	8.5
Volume acid added (ml)	400	400
Species		
Ca (mg/l)[a]	1100	1100
Ag	<0.5	<0.5
As	12	16
Ba	140	340
Cd	<0.1	0.3
Cr	14	9.3
Hg	<1.0	1.0
Pb	32	15
Se	<5.0	13
F^- (mg/l)	Acetate interference	
Cl^- (mg/l)	Acetate interference	
SO_4^{2-} (mg/l)	630	470

[a]Analyzed by flame AAS.

TABLE A-5. CONCENTRATIONS OF INORGANIC SPECIES IN OIL SHALE LEACHATE GENERATED BY THE CAE

	First replicate		Second replicate	
Final pH	6.64		6.58	
Species	Preserved	Reserve	Preserved	Reserve
Ca (mg/l)[a]	170	130	180	160
Ag	0.6	0.5	0.6	0.5
As	85	89	82	87
Ba	250	240	270	260
Cd	0.4	0.7	0.2	0.3
Cr	1.4	1.0	<1.0	<1.0
Hg	<1.0	<1.0	<1.0	1.2
Pb	7.1	6.1	5.7	5.6
Se	66	59	63	60
F^- (mg/l)	5.0		4.7	
Cl^- (mg/l)	2.1		2.1	
SO_4^{2-} (mg/l)	780		910	

[a]Analyzed by flame AAS.

TABLE A-6. CONCENTRATIONS OF INORGANIC SPECIES IN FBC WASTE LEACHATE GENERATED BY THE ASTM-A METHOD

	First replicate		Second replicate	
Final pH	12.52		12.54	
Species	Preserved	Reserve	Preserved	Reserve
Ca (mg/l)[a]	960	930	1000	1020
Ag	<0.5	<0.5	<0.5	<0.5
As	37	33	34	33
Ba[a]	<400	<400	<400	<400
Cd	0.4	0.3	0.4	0.4
Cr	62	58	29	34
Hg	<1.0	<1.0	<1.0	<1.0
Pb	9.0	7.9	12	10
Se	40	44	40	42
F^- (mg/l)	1.2		1.2	
Cl^- (mg/l)	5.0		7.5	
SO_4^{2-} (mg/l)	950		1230	

[a]Analyzed by flame AAS.

TABLE A-7. CONCENTRATIONS OF INORGANIC SPECIES IN FBC WASTE LEACHATE GENERATED BY THE ASTM-B METHOD[a]

Species	
Ca (mg/l)[b]	2700
Ag	<0.5
As	63
Ba	54
Cd	17
Cr	110
Hg	<1.0
Pb	<1.0
Se	<5.0
F^- (mg/l)	Acetate interference
Cl^- (mg/l)	Acetate interference
SO_4^{2-} (mg/l)	510

[a]Final pH: 11.94.

[b]Analyzed by flame AAS.

TABLE A-8. CONCENTRATIONS OF INORGANIC SPECIES IN FBC WASTE LEACHATE GENERATED BY THE EP

	First replicate	Second replicate
Initial pH	12.47	12.52
Final pH	12.28	12.32
Volume acid added (ml)	400	400

Species	Preserved	Reserve	Preserved	Reserve
Ca[a] (mg/1)	2800	2800	2800	2800
Ag	<0.5	<0.5	<0.5	<0.5
As	8.5	6.3	6.7	6.3
Ba	360	310	380	350
Cd	0.2	2.5	0.9	2.3
Cr	12	38	15	40
Hg	<1.0	1.2	1.0	1.3
Pb	8.2	9.9	10	12.6
Se	12	13	12	13
F^- (mg/1)	Acetate interference			
Cl^- (mg/1)	Acetate interference			
SO_4^{2-} (mg/1)	850		1280	

[a]Analyzed by flame AAS.

TABLE A-9. CONCENTRATIONS OF INORGANIC SPECIES IN FBC WASTE LEACHATE GENERATED BY THE CAE[a]

Species	Preserved	Reserve
Ca[b] (mg/1)	270	190
Ag	0.6	0.5
As	25	30
Ba	71	83
Cd	<0.1	0.2
Cr	16.7	17.1
Hg	<1.0	1.2
Pb	5.8	4.1
Se	28	40
F^- (mg/1)	0.6	
Cl^- (mg/1)	3.0	
SO_4^{2-} (mg/1)	160	

[a]Final pH: 11.74.

[b]Analyzed by flame AAS.

TABLE A-10. CONCENTRATIONS OF INORGANIC SPECIES IN BITUMINOUS COAL FLY ASH NO. 1 LEACHATE GENERATED BY THE ASTM-A METHOD[a]

Ca[b] (mg/1)	190
Ag[b]	<60
As	370
Ba[b]	<400
Cd[b]	<25
Cr[b]	<100
Hg	1.0
Pb[b]	<500
Se	160[c]
F^- (mg/1)	1.0
Cl^- (mg/1)	1.0
SO_4^{2-} (mg/1)	260

[a]Final pH: 10.4.

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

TABLE 11. CONCENTRATIONS OF INORGANIC SPECIES IN BITUMINOUS COAL FLY ASH NO. 1 LEACHATE GENERATED BY THE ASTM-B METHOD[a]

Ca[b] (mg/1)	270
Ag[b]	<60
As	2430[c]
Ba[b]	<400
Cd[b]	<25
Cr[b]	300
Hg	<1.0
Pb	<500
Se	140[c]
F^- (mg/1)	d
Cl^- (mg/1)	d
SO_4^{2-}	300

[a]Final pH: 4.5.

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

[d]Acetate interference.

TABLE A-12. CONCENTRATIONS OF INORGANIC SPECIES IN BITUMINOUS COAL FLY ASH NO. 1 LEACHATE GENERATED BY THE EP

	First replicate	Second replicate	Third replicate
Initial pH	8.9	9.0	8.3
Final pH	5.0	5.0	5.0
Volume acid added (ml)	15.7	22.9	24.4
Ca[a] (mg/l)	108	158	161
Ag[a]	<60	<60	<60
As	1120[b]	1440[b]	1830[b]
Ba[a]	<400	<400	<400
Cd[a]	<25	<25	<25
Cr[a]	<100	<100	<100
Hg	<1.0	<1.0	<1.0
Pb[a]	<500	<500	<500
Se	110[b]	140[b]	45
F^- (mg/l)	[c]	[c]	[c]
Cl^- (mg/l)	[c]	[c]	[c]
SO_4^{2-} (mg/l)	180	200	210

[a]Analyzed by flame AAS.

[b]Exceeds RCRA criteria.

[c]Acetate interference.

TABLE A-13. CONCENTRATIONS OF INORGANIC SPECIES IN BITUMINOUS COAL FLY ASH NO. 2 LEACHATE GENERATED BY THE ASTM-B METHOD

	Run 1 (60 cycles/min)[a]	Run 2 (120 cycles/min)[a]
Final pH	3.28	3.51
Species		
Ca[b] (mg/l)	600	540
Ag	44	26
As	4300[c]	4500[c]
Ba	95	110
Cd	400	480
Cr	11,400[c]	11,500[c]
Hg	<1.0	<1.0
Pb	600[c]	930[c]
Se	<5.0	<5.0
F^- (mg/l)	Acetate interference	
Cl^- (mg/l)	Acetate interference	
SO_4^{2-} (mg/l)	10,300	11,400

[a] Agitation rate.

[b] Analyzed by flame AAS.

[c] Exceeds RCRA criteria.

TABLE A-14. CONCENTRATIONS OF INORGANIC SPECIES IN BITUMINOUS COAL FLY ASH NO. 2 LEACHATE GENERATED BY THE CAE

	First replicate (120 cycles/min)[a]		Second replicate (120 cycles/min)[a]	
Final pH	3.11		3.08	
Species	Preserved	Reserve	Preserved	Reserve
Ca[b] (mg/l)	430	420	370	370
Ag	2.5	1.9	2.5	2.1
As	1320[c]	1280[c]	1270[c]	1310[c]
Ba	240	270	220	230
Cd	140	140	140	140
Cr	2150[c]	2090[c]	1810[c]	1740[c]
Hg	<1.0	<1.0	1.2	1.5
Pb	140	100	130	150
Se	33	32	31	34
F^- (mg/l)	9.3		11.0	
Cl^- (mg/l)	6.7		6.1	
SO_4^{2-} (mg/l)	2830		2740	

[a]Agitation rate.

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

TABLE A-15. CONCENTRATIONS OF INORGANIC SPECIES IN BOILER SLAG LEACHATE GENERATED BY THE ASTM-A METHOD[a]

Species	Preserved	Reserve
Ca[b] (mg/l)	1.5	1.8
Ag	<0.5	<0.5
As	<1.0	<1.0
Ba[b]	<400	<400
Cd	<0.1	<0.1
Cr	<1.0	<1.0
Hg	<1.0	<1.0
Pb	<1.0	<1.0
Se	<5.0	7.9
F^- (mg/l)	<1.0	
Cl^- (mg/l)	<1.0	
SO_4^{2-} (mg/l)	12	

[a]Final pH: 3.55.

[b]Analyzed by flame AAS.

TABLE A-16. CONCENTRATIONS OF INORGANIC SPECIES IN BOILER SLAG LEACHATE GENERATED BY THE ASTM-B METHOD[a]

Species	
Ca[b] (mg/l)	7.1
Ag	<0.5
As	24
Ba	29
Cd	3.8
Cr	4.4
Hg	<1.0
Pb	<1.0
Se	<5.0
F^- (mg/l)	Acetate interference
Cl^- (mg/l)	Acetate interference
SO_4^{2-} (mg/l)	33

[a]Final pH: 4.27.

[b]Analyzed by flame AAS.

TABLE A-17. CONCENTRATIONS OF INORGANIC SPECIES IN BOILER SLAG LEACHATE GENERATED BY THE CAE[a,b]

Species	Preserved	Reserve
Ca[c] (mg/l)	0.6	0.6
Ag	<0.5	<0.5
As	<1.0	<1.0
Ba	12.0	14
Cd	<0.1	<0.1
Cr	<1.0	<1.0
Hg	1.2	1.0
Pb	<1.0	<1.0
Se	<5.0	<5.0
F^- (mg/l)	<1.0	
Cl^- (mg/l)	1.5	
SO_4^{2-} (mg/l)	4.1	

[a]Final pH: 4.22.

[b]Agitated at 120 cycles/min.

[c]Analyzed by flame AAS.

TABLE A-18. CONCENTRATIONS OF INORGANIC SPECIES IN SCRUBBER SLUDGE LEACHATE GENERATED BY THE ASTM-A METHOD[a]

Ca[b] (mg/l)	580
Ag[b]	<60
As	150
Ba[b]	<400
Cd[b]	<25
Cr[b]	<100
Hg	<1.0
Pb[b]	<500
Se	120[c]
F^- (mg/l)	<1.0
Cl^- (mg/l)	2.1
SO_4^{2-} (mg/l)	1960

[a]Final pH: 5.0

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

TABLE A-19. CONCENTRATIONS OF INORGANIC SPECIES IN SCRUBBER SLUDGE LEACHATE GENERATED BY THE ASTM-B METHOD[a]

Ca^{b} (mg/l)	690
Ag^{b}	<60
As	350
Ba^{b}	<400
Cd^{b}	<25
Cr^{b}	<100
Hg	1.0
Pb^{b}	<500
Se	130[c]
F^{-} (mg/l)	d
Cl^{-} (mg/l)	d
SO_4^{2-} (mg/l)	2260

[a]Final pH: 4.5.

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

[d]Acetate interference.

TABLE A-20. CONCENTRATIONS OF INORGANIC SPECIES IN SCRUBBER SLUDGE LEACHATE GENERATED BY THE EP[a]

Ca^{b} (mg/l)	510
Ag^{b}	<60
As	140
Ba^{b}	<400
Cd^{b}	<25
Cr^{b}	<100
Hg	<1.0
Pb^{b}	<500
Se	110[c]
F^{-} (mg/l)	d
Cl^{-} (mg/l)	d
SO_4^{2-} (mg/l)	1300

[a]Initial pH: 5.6
Final pH: 5.1
Volume acid added (ml): 13.5

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

[d]Acetate interference.

TABLE 21. CONCENTRATIONS OF INORGANIC SPECIES IN SCRUBBER SLUDGE LEACHATE GENERATED BY THE CAE[a]

Species	Preserved	Reserve
Ca^{b} (mg/l)	600	620
Ag	1.0	0.8
As	160	170
Ba	73	77
Cd	1.4	1.3
Cr	1.2	1.4
Hg	<1.0	1.4
Pb	13.9	14.2
Se	150[c]	120[c]
F^{-} (mg/l)	2.2	
Cl^{-} (mg/l)	3.9	
SO_4^{2-} (mg/l)	1480	

[a]Final pH: 5.43.

[b]Analyzed by flame AAS.

[c]Exceeds RCRA criteria.

TABLE 22. CONCENTRATIONS OF INORGANIC SPECIES IN HOPPER ASH LEACHATE GENERATED BY THE ASTM-A METHOD

	First replicate	Second replicate	Third replicate
Final pH	12.13	12.16	12.16
Species			
Ca^{a} (mg/l)	470	490	430
Ag	<0.5	<0.5	<0.5
As	27	27	24
Ba	1870	2250	1810
Cd	<0.1	0.1	<0.1
Cr	120	120	110
Hg	<1.0	<1.0	<1.0
Pb	7.7	7.9	8.5
Se	410[b]	550[b]	470[b]
F^- (mg/l)	9.6	9.7	9.8
Cl^- (mg/l)	1.0	1.0	1.0
SO_4^{2-} (mg/l)	150	190	200

[a]Analyzed by flame AAS.

[b]Exceeds RCRA criteria.

TABLE A-23. CONCENTRATIONS OF INORGANIC SPECIES IN HOPPER ASH LEACHATE GENERATED BY THE ASTM-B METHOD

	First replicate	Second replicate	Third replicate
Final pH	11.03	11.04	11.02
Species			
Ca^{a} (mg/l)	2300	2200	2200
Ag	<0.5	<0.5	<0.5
As	70	70	60
Ba	120	130	130
Cd	6.8	4.9	6.9
Cr	540[b]	510[b]	490[b]
Hg	<1.0	<1.0	<1.0
Pb	<1.0	<1.0	<1.0
Se	1460[b]	1930[b]	1700[b]
F^- (mg/l)	Acetate interference		
Cl^- (mg/l)	Acetate interference		
SO_4^{2-} (mg/l)	2450	2100	1720

[a]Analyzed by flame AAS.

[b]Exceeds RCRA criteria.

TABLE A-24. CONCENTRATIONS OF INORGANIC SPECIES IN HOPPER ASH LEACHATE GENERATED BY THE EP

	First replicate	Second replicate	Third replicate
Initial pH	12.05	12.03	12.00
Final pH	9.44	10.37	10.22
Volume acid added (ml)	400	400	400
Species			
Ca[a] (mg/l)	2200	2200	2200
Ag	<0.5	<0.5	<0.5
As	15	30	17
Ba	210	180	170
Cd	0.5	0.1	0.1
Cr	190	150	330
Hg	<1.0	<1.0	<1.0
Pb	13	14	17
Se	200[b]	150[b]	150[b]
F^- (mg/l)	Acetate interference		
Cl^- (mg/l)	Acetate interference		
SO_4^{2-} (mg/l)	670	450	550

[a]Analyzed by flame AAS.

[b]Exceeds RCRA criteria.

TABLE A-25. CONCENTRATIONS OF INORGANIC SPECIES IN HOPPER ASH LEACHATE GENERATED BY THE CAE

	First replicate	Second replicate	Third replicate
Final pH	7.30	7.25	7.33
Species			
Ca[a] (mg/l)	190	210	210
Ag	<0.5	<0.5	<0.5
As	89	110	110
Ba	710	710	700
Cd	0.4	0.6	0.4
Cr	180	210	200
Hg	<1.0	<1.0	<1.0
Pb	8.4	8.0	8.2
Se	350[b]	470[b]	500[b]
F^- (mg/l)	2.0	2.1	3.3
Cl^- (mg/l)	1.6	1.6	1.5
SO_4^{2-}	250	280	300

[a]Analyzed by flame AAS.

[b]Exceeds RCRA criteria.

APPENDIX B

SPARK SOURCE MASS SPECTROGRAPHY DATA FOR THE EP LEACHATE OF BITUMINOUS COAL FLY ASH NO. 1 AND THE EP LEACHATE BLANK

TABLE B-1. SSMS DATA FOR THE EP LEACHATE OF BITUMINOUS COAL FLY ASH NO. 1

Element	Concentration (µg/ml)	Element	Concentration (µg/ml)
Uranium	ND[a]	Ruthenium	ND
Thorium	ND	Molybdenum	0.14
Bismuth	ND	Niobium	ND
Lead	ND	Zirconium	ND
Thallium	ND	Yttrium	ND
Mercury	NR[b]	Strontium	0.88
Gold	ND	Rubidium	0.037
Platinum	NR	Bromine	0.033
Iridium	ND	Selenium	0.069
Osmium	ND	Arsenic	0.49
Rhenium	ND	Germanium	0.80
Tungsten	ND	Gallium	ND
Tantalum	NR	Zinc	0.16
Hafnium	ND	Copper	0.069
Lutecium	ND	Nickel	0.15
Ytterbium	ND	Cobalt	0.022
Thulium	ND	Iron	0.023
Erbium	ND	Manganese	0.14
Holmium	ND	Chromium	0.003
Dysprosium	ND	Vanadium	0.35
Terbium	ND	Titanium	0.065
Gadolinium	ND	Scandium	NR
Europium	ND	Calcium	210
Samarium	ND	Potassium	11
Neodymium	ND	Chlorine	0.23
Praseodymium	ND	Sulphur	5.7
Cerium	ND	Phosphorus	0.94
Lanthanum	ND	Silicon	4.4
Barium	0.12	Aluminum	0.28
Cesium	0.005	Magnesium	4.8
Iodine	0.007	Sodium	4.9
Tellurium	ND	Fluorine	0.032
Antimony	0.043	Oxygen	NR
Tin	ND	Nitrogen	NR
Indium	IS[c]	Carbon	NR
Cadmium	0.001	Boron	0.084
Silver	NR	Beryllium	<0.001
Palladium	ND	Lithium	0.10
Rhodium	ND		

[a] ND - not detected.

[b] NR - not reported.

[c] IS - internal standard.

TABLE B-2. SSMS DATA FOR THE EP LEACHATE BLANK

Element	Concentration (µg/ml)	Element	Concentration (µg/ml)
Uranium	<0.005	Ruthenium	<0.001
Thorium	<0.006	Molybdenum	0.003
Bismuth	<0.002	Niobium	<0.001
Lead	<0.003	Zirconium	<0.002
Thallium	<0.002	Yttrium	<0.001
Mercury	NR[a]	Strontium	<0.001
Gold	<0.001	Rubidium	<0.001
Platinum	NR	Bromine	<0.002
Iridium	<0.002	Selenium	<0.001
Osmium	<0.002	Arsenic	<0.001
Rhenium	<0.001	Germanium	<0.004
Tungsten	<0.008	Gallium	<0.001
Tantalum	NR	Zinc	0.005
Hafnium	<0.014	Copper	0.011
Lutecium	<0.002	Nickel	0.056
Ytterbium	<0.013	Cobalt	0.002
Thulium	<0.001	Iron	0.058
Erbium	<0.003	Manganese	0.019
Holmium	<0.001	Chromium	0.004
Dysprosium	<0.004	Vanadium	<0.001
Terbium	<0.001	Titanium	0.004
Gadolinium	<0.006	Scandium	NR
Europium	<0.002	Calcium	0.23
Samarium	<0.004	Potassium	0.11
Neodymium	<0.004	Chlorine	0.031
Praseodymium	<0.001	Sulphur	0.004
Cerium	<0.002	Phosphorus	0.002
Lanthanum	<0.001	Silicon	0.28
Barium	0.007	Aluminum	0.038
Cesium	<0.001	Magnesium	0.009
Iodine	0.007	Sodium	0.43
Tellurium	<0.001	Fluorine	0.000
Antimony	<0.001	Oxygen	NR
Tin	<0.001	Nitrogen	NR
Indium	IS[b]	Carbon	NR
Cadmium	<0.001	Boron	0.000
Silver	NR	Beryllium	<0.001
Palladium	<0.001	Lithium	0.000
Rhodium	<0.001		

[a] NR - not reported.

[b] IS - internal standard.

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Center for Environmental Research Information
Cincinnati, Ohio 45268

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE. $300
AN EQUAL OPPORTUNITY EMPLOYER

POSTAGE AND FEES PAID
U S ENVIRONMENTAL PROTECTION AGENCY
EPA-335

If your address is incorrect, please change on the above label tear off; and return to the above address.
If you do not desire to continue receiving these technical reports, CHECK HERE ☐; tear off label, and return it to the above address,

Publication No. EPA-600/7-80-118